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A TREATISE ON CHEMISTRY.

A

TREATISE ON CHEMISTRY

BY

SIR H. E. ROSCOE F.R.S. AND C. SCHORLEMMER F.R.S.

VOLUME III

THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES,

OR

ORGANIC CHEMISTRY

PART V

"*Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723.

A. W. Palmer
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PREFACE TO VOL III., PART V.

The Fifth Part of the Treatise on Organic Chemistry contains a description of the Benzene-Hydrocarbons and their Derivatives with eight and more than eight atoms of Carbon, and concludes with the group of the Terpenes and Camphors, including Indiarubber and Guttapercha. Like the preceding parts it forms a chapter in itself. The authors are much indebted to Dr. A. Harden for the assistance which he has given them in passing this volume through the press.

H. E. R.
C. S.

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ORGANIC CHEMISTRY.

ORGANIC CHEMISTRY,

OR THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES.

PART V.

STYROLENE GROUP.

Ethylbenzene, $C_6H_5.C_2H_5$.

2274 This substance was first prepared by Fittig and Tollens by the action of sodium on a mixture of bromobenzene and ethyl bromide,[1] and is also formed when ethylene is passed into a heated mixture of benzene and aluminium chloride,[2] and in small quantities, when benzene is heated to 100° with ethyl ether and zinc chloride.[3] It has likewise been obtained by a remarkable reaction from toluene, which on heating with aluminium chloride in an open vessel yields a mixture of hydrocarbons consisting entirely of ethylbenzene and the three xylenes. These cannot be separated by fractional distillation, but their amounts can be determined by a method which is more fully described below.[4] In order to explain its formation, it may be assumed that the toluene is resolved into benzene and methylene, one portion of the latter combining with toluene to form the xylenes, while the remainder is polymerized to ethylene, which combines with the benzene with formation of ethylbenzene (Pt. IV. p. 202).

[1] *Ann. Chem. Pharm.* cxxxi. 310; Fittig and König, *Ibid.* cxliv. 277.
[2] Bahlson, *Bull. Soc. Chim.* xxxi. 540.
[3] Bahlson, *ibid.* xxxii. 618.
[4] Friedel and Crafts, *Compt. Rend.* ci. 1218.

Ethylbenzene is a liquid possessing a smell like that of toluene; it boils at 136·5° and has a sp. gr. of 0·8664 at 22·5°. It is oxidized to benzoic acid by dilute nitric acid or chromic acid, while when a solution of chromium trioxide in glacial acetic acid is employed, a little methylphenylketone is always formed.[1] Ethylbenzene also occurs, together with toluene in bone-oil.[2]

α-Ethylphenol, $C_6H_4(C_2H_5)OH$, is formed by fusing *α*-ethylbenzenesulphonic acid with caustic potash.[3] It smells precisely like ordinary phenol, boils at 214°-215° and crystallizes in needles or transparent prisms, which melt at 47°-48°, and are readily soluble in alcohol, and to some extent in water; the solution is coloured a dirty greyish blue by ferric chloride. It decomposes into ethylene and phenol when heated with phosphorus pentoxide.[4]

β-Ethylphenol has been prepared from *β*-ethylbenzenesulphonic acid (Beilstein and Kuhlberg) and from crude nitroethyl benzene, the reduction product of this being treated in hydrochloric acid solution with potassium nitrite.[5] It is a liquid, which boils at 212°, does not solidify at −18°, and gives a greenish blue colouration with ferric chloride. It is converted into salicylic acid by fusion with caustic potash.

This ethylphenyl, together with other products, is formed, according to Auer, when a mixture of absolute alcohol and phenol is heated with zinc chloride.[6] Errera has, however, shown that a mixture of ethylphenols is thus obtained, in which the *α*-compound predominates.[7]

The *phlorol*, which Hlasiwetz obtained by the distillation of phloretinic acid, $C_8H_8(OH)CO_2H$, with lime,[8] is, according to Oliveri, identical with *β*-ethylphenol. On heating it with methyl iodide, caustic potash, and wood-spirit, he obtained the methyl ether, $C_6H_4(C_2H_5)OCH_3$, as a strongly refractive liquid boiling at 185°.[9] A compound of the same formula was found by Ciamician among the products of distillation of gum-ammoniac with zinc dust; it boils at about 190°-192°, and yields

[1] Friedel and Bahlson, *Bull. Soc. Chim.* xxxiii. 615.
[2] Weidel and Ciamician, *Ber. Deutsch. Chem. Ges.* xiii. 70.
[3] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clvi. 211; Fittig and Kiesow, *ibid.* clvi. 251.
[4] Chrustchow, *Ber. Deutsch. Chem. Ges.* vii. 1166.
[5] Suida and Plohn, *Monatsh. Chem.* i. 175.
[6] *Ber. Deutsch. Chem. Ges.* xvii. 619.
[7] *Ibid.* xviii. Ref. 150.
[8] *Ann. Chem. Pharm.* cii. 166.
[9] *Ber. Deutsch. Chem. Ges.* xvi. 1879.

a phenol, which, since it boils at 220° and is converted into salicylic acid by fusion with caustic potash,[1] is probably impure β-ethylphenol.

The isobutyric ether of an isomeric phenol, boiling at 224°-225°, occurs in the ethereal oil from the root of *Arnica montana*.[2] This is probably meta-ethylphenol, since the oil also contains methylthymol, $C_6H_4(OCH_3)C_3H_7$, which belongs to the meta-series. β-Ethylphenol is certainly the ortho-compound, and the solid ethylphenol must therefore be the para-compound.

2275 *Chlorethylbenzene*, $C_6H_4(C_2H_5)Cl$. When ethylene is passed into a heated mixture of chlorobenzene and aluminium chloride, all the hydrogen atoms of the chlorobenzene are gradually replaced by ethyl; the first product consists of a mixture of the three chlorethylbenzenes, in which the meta-compound predominates, and which is a pleasant smelling liquid, boiling at 179°-182°. On oxidation with chromic acid it yields meta- and para-chlorobenzoic acids, while orthochlorobenzoic acid is also formed by the action of potassium permanganate.[3]

Paradichlorethylbenzene, $C_6H_3(C_2H_5)Cl_2$, is obtained in a similar manner from paradichlorobenzene. It is a liquid which has a pleasant odour and boils at 213·5°.[4]

Bromethylbenzene, $C_6H_4(C_2H_5)Br$, is formed by the action of bromine, which contains iodine, on well-cooled ethylbenzene.[5] It is a colourless liquid which has an aromatic odour, boils at 199°, and is converted by oxidation into parabromobenzoic acid.

Dibromethylbenzene, $C_6H_3(C_2H_5)Br_2$, is prepared by the further action of bromine in the presence of iodine, on the preceding compound. It is a liquid which mixes in almost every proportion with petroleum spirit, boiling at 80°-90° (Friedel and Crafts).

Pentabromethylbenzene, $C_6Br_5.C_2H_5$, is formed when dibrom-ethylbenzene is treated with bromine and aluminium chloride or bromide. It crystallizes in monosymmetric prisms, which dissolve at 20° in 11 parts of petroleum spirit, melts at 141·5°, and can only be distilled under diminished pressure.

By means of this compound Friedel and Crafts have determined the amount of ethylbenzene which is formed by heating toluene with aluminium chloride. When the fraction of the product

[1] *Ber. Deutsch. Chem. Ges.* xii. 1658.
[2] Sigel, *Ann. Chem. Pharm.* clxx. 354.
[3] Istrati, *Ann. Chim. Phys.* [6] vi. 395.
[4] *Ann. Chim. Phys.* [6] vi. 475.
[5] Fittig and König, *loc. cit.*; Thorpe, *Zeitschr. Chem.* 1871, 131; Schramm, *Ber. Deutsch. Chem. Ges.* xviii. 350.

which boils at 138° is treated with bromine containing 1 per cent. of iodine, the xylenes are converted into tetrabromoxylenes, which dissolve in about 200 parts of petroleum spirit, while the ethylbenzene yields the dibromo-compound, which, as already stated, is extremely soluble in petroleum spirit; this is freed as completely as possible from the xylene derivatives and is then converted into the pentabromo-compound and weighed. They thus found that the fraction boiling at 138° contains 10 per cent. of ethylbenzene.

Paranitro-ethylbenzene, $C_6H_4(C_2H_5)NO_2$, is formed, together with the ortho-compound, when ethylbenzene is dissolved in nitric acid of sp. gr. 1·475; it is a yellow liquid which boils at 245°-246° and is converted into paranitrobenzoic acid by oxidation.

Orthonitro-ethylbenzene boils at 227°-228° and is not attacked by chromic acid solution.[1]

Ethylbenzenesulphonic acid, $C_6H_4(C_2H_5)SO_3H$, is formed in two modifications when ethylbenzene is dissolved in slightly fuming sulphuric acid. They both form potassium salts which crystallize well and can readily be separated, since that of the *a*-acid, which is the chief product, is much less soluble than that of the *β*-acid.[2]

Paramidoethylbenzene, $C_6H_4(C_2H_5)NH_2$, is obtained by the reduction of paranitro-ethylbenzene,[3] and is also formed when ethylaniline hydrochloride is heated to 300°.[4] It is a liquid, which boils at 213°-214° and forms a difficultly soluble sulphate.

Orthamido-ethylbenzene boils at 210°-211° (Beilstein and Kuhlberg).

STYROLYL COMPOUNDS.

2276 *Primary Styrolyl alcohol*, $C_6H_4.C_2H_4.OH$. This compound which is also known as *phenylethyl alcohol* or *benzyl carbinol*, was first prepared by Radziszewski from phenylacetaldehyde, $C_6H_5.CH_2.CHO$, which was dissolved in dilute alcohol and treated with sodium amalgam, the solution being kept neutral by the addition of sulphuric acid. It is a liquid which only possesses a faint odour and boils at 212°.[5]

[1] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clvi. 206.
[2] Chrustchow, *Ber. Deutsch. Chem. Ges.* vii. 1165.
[3] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clvi. 206.
[4] Hofmann, *Ber. Deutsch. Chem. Ges.* vii. 526.
[5] *Ibid.* ix. 372.

Primary styrolyl chloride, $C_6H_5.C_2H_4Cl$, is formed by the action of chlorine on boiling ethylbenzene, and is a liquid which boils at 200°-204°, the larger portion being thus resolved into hydrochloric acid and styrolene, $C_6H_5.C_2H_3$. This decomposition renders it probable that the secondary chloride has been simultaneously formed, as is the case with the paraffins. Phenylpropionitril, $C_6H_4.C_2H_4.CN$, is produced when the chloride is heated with potassium cyanide and alcohol.[1]

Styrolyl acetate, $C_6H_5.C_2H_4.O.C_2H_3O$, is obtained by heating the alcohol to 150° with acetic anhydride. It is a liquid which has a pleasant odour and boils at 224°.

Styrolylamine, $C_6H_5.C_2H_4.NH_2$. This base, which is also named *phenylethylamine*, was first prepared by Fileti by the action of zinc and hydrochloric acid on cherry laurel oil, which chiefly consists of phenylhydroxyacetonitril, $C_6H_5.CH(OH)CN$. He also prepared it by the same method from amygdalin, the glucoside of this nitril,[2] while Bernthsen [3] and Spica [4] obtained it from phenylacetonitril, which can also be readily converted into the amine by the addition of sodium to its alcoholic solution (Ladenburg).[5]

It is also a product of the dry distillation of phenylalanine,[6] $C_6H_5.C_2H_3.(NH_2)CO_2H$, and forms a liquid possessing an unpleasant ammoniacal odour. It boils at 193°, dissolves slightly in water, more readily in alcohol, has a strongly alkaline reaction and is rapidly changed by exposure to the air into the crystalline carbonate, which was mistaken by Bernthsen for the free base. Its hydrochloride decomposes on heating into ammonium chloride, styrolene and distyrolylamine.[7]

Distyrolylamine, $(C_6H_5.C_2H_4)_2NH$, is formed simultaneously with the primary and tertiary bases by the action of zinc and hydrochloric acid on phenylacetonitril (Spica):

$$C_6H_5.CH_2.CH_2.NH_2 + C_6H_5.CH_2.CN + 4H = (C_6H_5.CH_2.CH_2)_2NH + NH_3.$$

It is a liquid which boils at 335°-337° under a pressure of 603 mm. and is slightly soluble in water, forming a solution which is

[1] Fittig and Kiesow, *Ann. Chem. Pharm.* clvi. 245.
[2] *Ber. Deutsch. Chem. Ges.* xii. 296.
[3] *Ann. Chem. Pharm.* clxxxiv. 304.
[4] *Ber. Deutsch. Chem. Ges.* xiii. 204; *Gaz. Chim. ital.* ix. 555.
[5] *Ber. Deutsch. Chem. Ges.* xix. 782.
[6] Erlenmeyer and Lipp, *Ann. Chem. Pharm.* ccxix. 202.
[7] Fileti and Piccini, *Ber. Deutsch. Chem. Ges.* xii. 1308, 1700.

alkaline to litmus. It readily forms salts with acids, but seems not to absorb carbon dioxide from the air.

Tristyrolylamine, $(C_6H_5.C_2H_4)_3N$, is an oily liquid, almost insoluble in water, but forming an alkaline solution in alcohol.

Parahydroxystyrolylamine, $C_6H_4(OH)C_2H_4.NH_2$. This compound, which has also received the name of *ethyloxyphenylamine*, is formed as a crystalline sublimate when tyrosine, $C_6H_4(OH)CH_2.CH(NH_2)CO_2H$, is heated to 270°.[1] It is only slightly soluble in water, has a strongly alkaline reaction, and yields ammonia and parahydroxybenzoic acid on fusion with potash.[2]

2277 *Secondary styrolyl alcohol* or *methylphenylcarbinol*, $C_6H_5.CH(OH)CH_3$, was first prepared by Emmerling and Engler, who obtained it by the action of sodium amalgam on a solution of methylphenylketone in dilute alcohol,[3] and was then prepared by Radziszewski from the acetate which is described below.[4] It is a strongly refractive liquid which boils at 202°-203° and has a very disagreeable odour.

Secondary styrolyl ethyl ether, $C_6H_5CH(OC_2H_5)CH_3$, was obtained by Thorpe as a pleasant smelling liquid by heating the bromide with alcoholic ammonia; it boils at 185°-187°.[5]

Secondary styrolyl chloride, $C_6H_5.CHCl.CH_3$, is formed when hydrochloric acid gas is passed into the alcohol,[6] and, together with acetic acid, when the alcohol is treated with acetyl chloride (Radziszewski). It is a liquid which boils with decomposition at 194°.

Secondary styrolyl bromide, $C_6H_5.CHBr.CH_3$, is obtained by the action of bromine on boiling ethylbenzene,[7] which is therefore attacked by chlorine and bromine in exactly the same manner as the paraffins (Part I. p. 135). It may also be prepared by the action of hydrobromic acid on the alcohol. It is a strongly refractive liquid, which is to a large extent resolved into hydrobromic acid and styrolene by distillation at the ordinary pressure, but boils at 148°-152° without decomposition under a pressure of 500 mm. (Thorpe).

Secondary styrolylacetate, $C_6H_5.CH(O.CO.CH_3)CH_3$, was prepared by Radziszewski from the bromide by the action of silver

[1] Schmitt and Nasse, *Ann. Chem. Pharm.* cxxxiii. 214.
[2] Barth, *ibid.* clii. 101.
[3] *Ber. Deutsch. Chem. Ges.* vi. 1005.
[4] *Ibid.* vii. 140.
[5] *Zeitschr. Chem.* 1871, 131.
[6] Engler and Bethge, *Ber. Deutsch. Chem. Ges.* vii. 1127.
[7] Berthelot, *Bull. Soc. Chim.* x. 343.

acetate and glacial acetic acid. It is a liquid which has a pleasant odour, resembling that of jasmine, and boils at 217°-220° (Thorpe), at which temperature it is partially resolved into styrolene and acetic acid.

Secondary styrolylamine, $C_6H_5CH(NH_2)CH_3$, is readily formed by the action of sodium amalgam and glacial acetic acid upon an alcoholic solution of phenylhydrazine-acetophenone :

$$\begin{matrix} CH_3 \\ C_6H_5 \end{matrix}\!\!>\!C{=}N{-}NH.C_6H_5 + 4H = \begin{matrix} CH_3 \\ C_6H_5 \end{matrix}\!\!>\!CH.NH_2 + NH_2.C_6H_5.$$

In order to separate the bases, they are converted into the sulphates and treated in acid solution with sodium nitrite, until a small portion yields no aniline after neutralization with an alkali and extraction with ether, the aniline being recognized by the bleaching powder reaction. Secondary styrolylamine is an oily liquid which has a characteristic odour, boils at 182°-185°, and is tolerably soluble in water. The solution has a strongly alkaline reaction and deposits the base on the addition of concentrated caustic soda solution. It combines with acids to form salts which crystallize well, and absorbs carbon dioxide from the air, with formation of a crystalline substance which melts at 96° and sublimes in stellate groups of needles. The phenylhydrazine derivatives of all other ketones and aldehydes behave in a similar manner to that of acetophenone, so that these oxygen compounds can be readily reduced to amines.[1]

PHENYLACETYL COMPOUNDS.

2278 *Phenylacetaldehyde*, $C_6H_5.CH_2.CHO$, was obtained by Cannizzaro by heating a mixture of calcium formate and calcium phenylacetate.[2] It is also formed when phenyl-lactic acid is heated with dilute sulphuric acid to 130° (Erlenmeyer) :

$$C_6H_5.CH_2.CH(OH)CO_2H = C_6H_5.CH_2.CHO + CH_2O_2.$$

This reaction corresponds exactly with the decomposition of ordinary lactic acid into acetaldehyde and formic acid.[3] It can

[1] Tafel, *Ber. Deutsch. Chem. Ges.* xix. 1924.
[2] *Ann. Chem. Pharm.* cxix. 253 ; cxxiv. 252 ; Radziszewski, *Ber. Deutsch. Chem. Ges.* ix. 372.
[3] *Ber. Deutsch. Chem. Ges.* xiii. 303.

more readily be prepared by boiling phenylbromolactic acid with sodium carbonate solution, or by distilling a solution of one molecule of phenylchlorolactic acid and two molecules of caustic soda with dilute sulphuric acid.[1] *β*-Phenylhydroxyacrylic acid,[2] $C_6H_5C(OH)=CH.CO_2H$, is an intermediate product of this reaction, and the aldehyde is therefore also obtained when the sodium salt of this (Erlenmeyer and Lipp) or that of the *α*-acid, $C_6H_5CH=C(OH)CO_2H$ (Plöchl), is distilled with dilute sulphuric acid. Phenylglyceric acid, $C_6H_5.CH(OH)CH(OH)CO_2H$, formed by the combination of the phenylacrylic acid with water, is a bye-product of all these reactions. Styrolene alcohol is then produced from the phenylacrylic acid by the elimination of carbon dioxide and readily changes into phenylacetaldehyde.

Etard obtained this substance from ethylbenzene, which like other aromatic hydrocarbons, combines with chromyl chloride to form phenylethidenedichlorochromic acid, which is decomposed by water with formation of the aldehyde:[3]

$$C_6H_5.CH_2.CH(OCrCl_2.OH)_2 + H_2O = C_6H_5.CH_2.CHO + 4HCl + 2CrO_2.$$

Phenylacetaldehyde is a liquid, which possesses a characteristic penetrating odour and boils at 203°-207°, a portion simultaneously losing water and being converted into a resinous mass. It forms a compound with acid sodium sulphite which crystallizes in small lustrous plates. Nitric acid oxidizes it to benzoic acid.

Paranitrophenylacetaldehyde, $C_6H_4(NO_2)CH_2.CHO$ is formed by boiling barium *β*-paranitrophenylchlorolactate with water:

$$(C_6H_4(NO_2)CHCl.CH(OH)CO_2)_2Ba = 2C_6H_4(NO_2)CH_2.CHO + 2CO_2 + BaCl_2.$$

It crystallizes from hot water in fascicular groups of needles melting at 85°—86°.[4]

2279 *Phenylacetic acid*, $C_6H_5.CH_2.CO_2H$. In the year 1856, Cannizzaro obtained an acid by heating benzyl chloride with potassium cyanide, and boiling the nitril thus formed with caustic potash, and considered it to be identical with the substance which Noad had previously prepared by the oxidation of

[1] Erlenmeyer and Lipp, *Ann. Chem. Pharm.* ccxix. 179; *Ber. Deutsch. Chem. Ges.* xiii. 308.
[2] Plöchl, *ibid.* xvi. 2815.
[3] *Ann. Chim. Phys.* [5] xxii. 248.
[4] Lipp, *Ber. Deutsch. Chem. Ges.* xix. 2647.

cymene[1] (Part IV. p. 418). An acid of the same composition was isolated by Strecker and Möller from the products obtained by boiling vulpinic acid with baryta water. They showed that this substance differs from Noad's acid, but is identical with Cannizzaro's compound and named it *alphatoluylic acid*. On account of its great similarity to benzoic acid, they assumed that it, and not Noad's toluylic acid, is the true homologue of benzoic acid,[2] while Cannizzaro came to the alternative conclusion. The latter chemist prepared the aldehydes of the two isomeric acids and found that tolualdehyde changes to toluic acid in the air as rapidly as oil of bitter almonds to benzoic acid, and that it is converted by alcoholic potash into toluylic acid and the corresponding alcohol. By the oxidation of alphatolualdehyde, on the other hand, he obtained an acid containing seven atoms of carbon, which appeared to be a mixture of benzoic and nitrobenzoic acids. Since Strecker and Möller had found that alphatoluylic acid is converted into benzaldehyde by oxidation, he concluded that Noad's toluic acid is the true homologue of benzoic acid, but that alphatoluic acid was still a member of the benzoic series.[3]

The isomerism of these acids was shortly afterwards explained by Kekulé in a simple manner. He says: "Toluic acid stands in the same relation to toluene as benzoic acid to benzene; it therefore contains two side-chains: CH_3 and CO_2H. Alphatoluic acid, on the other hand, contains a lengthened side-chain; the group CO_2H is connected with the carbon of the CH_3 side-chain:

$(C_6H_4.CH_3)CO_2H.$	$(C_6H_5)CH_2.CO_2H.$
Toluic Acid.	Alphatoluic Acid.

Toluic acid may therefore be designated methylphenylformic acid, and alphatoluic acid as phenylacetic acid.[4]

The latter acid was then prepared by Crum Brown from mandelic acid or phenylhydroxacetic acid, $C_6H_5.CH(OH)\ CO_2H$, by heating with hydriodic acid and phosphorus.[5] Kraut obtained it by fusing atropaic acid, $CH_2{=}C(C_6H_5)CO_2H$, with caustic potash,[6] and Zincke prepared it synthetically by heating bromobenzene to 180°—200° with ethylchloracetate and copper

[1] *Ann Chem. Pharm.* xcvi. 246.
[2] *Ibid.* cxiii. 64.
[3] *Ibid.* cxxiv. 252.
[4] *Ibid.* cxxxvii. 150.
[5] *Zeitschr. Chem.* 1865, 443.
[6] *Ann. Chem. Pharm.* cxlviii. 242.

powder.[1] E. and H. Salkowski found it among the products of the pancreatic putrefaction of albumen and wool.[2] In order to prepare it, 60 grms. of pure potassium cyanide are dissolved in 55 grms. of water, contained in a flask connected with an inverted condenser, and a mixture of 100 grms. of benzyl chloride and 100 grms. of alcohol gradually added to the warm solution, which is then boiled for three hours, freed from the upper layer and distilled. The portion which passes over below 236° is carefully added to a solution of 45 grms. of caustic potash in 25 grms. of water, and the mixture heated for 5-6 hours, until ammonia is no longer evolved, after which the alcohol is distilled off, the saline residue dissolved in as small a quantity of water as possible, and the phenylacetic acid precipitated in the filtered solution with hydrochloric acid.[3]

The nitril may be more simply decomposed by heating it with three times its weight of a mixture of three volumes of sulphuric acid and two of water in a flask provided with a wide conducting tube, bent twice at right angles, which passes into a flask containing water, the end of the tube being situated just above the surface of the water. The mixture is heated until bubbles of steam commence to be formed, the flame being then removed. A violent reaction soon sets in, a portion of the nitril passing over into the condenser. After cooling, the precipitated phenylacetic acid is filtered off and washed with water, the washings being subsequently extracted with ether.[4]

It can also be readily prepared from benzaldehyde; to this is added rather more than one molecule of pure potassium cyanide moistened with water, fuming hydrochloric acid being then gradually added with constant agitation. Phenylhydroxyacetonitril is thus formed, and is converted by heating to 130°—140°, with highly concentrated hydrochloric acid into phenylchloracetic acid, $C_6H_5.CHCl.CO_2H$, which is reduced by the action of zinc dust and ammonia in the cold to phenylacetic acid.[5]

Properties.—Phenylacetic acid is freely soluble in alcohol and ether, but only slightly in cold water, more readily in hot water, from which it separates in oily drops until the temper-

[1] *Ber. Deutsch. Chem. Ges.* ii. 737.
[2] *Ibid.* xii. 648.
[3] Mann, *ibid.* xiv. 1645.
[4] Städel, *ibid.* xix. 1949.
[5] Spiegel, *ibid.* xiv. 239.

ature has fallen below the melting point of the acid, after which it crystallizes in thin, iridescent, pointed plates, which resemble those of benzoic acid and belong to the rhombic system. It melts at 76·5°, sublimes below 100° and boils at 265·5°, forming an irritating vapour which produces coughing. On oxidation with manganese dioxide and dilute sulphuric acid it yields formic acid, benzaldehyde and benzoic acid.

2280 *The phenylacetates.* The salts of the metals of the alkalis and alkaline earths are very readily soluble.

Calcium phenylacetate, $(C_6H_5.CH_2.CO_2.)_2Ca + 3H_2O$, crystallizes in needles.

Silver phenylacetate, $C_6H_5.CH_2.CO_2Ag$, is a precipitate consisting of fine plates, which can be recrystallized from hot water. The copper salt is an amorphous green precipitate.

Methyl phenylacetate, $C_6H_5.CH_2.CO_2.CH_3$, is obtained by the action of hydrochloric acid on a solution of the acid in methyl alcohol, and is a liquid which possesses a faint but agreeable odour and boils at 220°.

Ethyl phenylacetate, $C_6H_5.CH_2.CO_2.C_2H_5$, is prepared in a similar manner[1] and also by the action of ethyl iodide on the potassium salt.[2] It boils at 226° and has a very pleasant odour. It is also formed when hydrochloric acid gas is passed into a heated alcoholic solution of phenylacetonitril.[3]

	Boiling-point.
Propyl phenylacetate, $C_6H_5.CH_2.CO_2.C_3H_7$	238°
Isobutyl phenylacetate, $C_6H_5.CH_2.CO_2.CH_2.CH(CH_3)_2$	247°
Benzyl phenylacetate,[4] $C_6H_5.CH_2.CO_2.CH_2.C_6H_5$ . .	318°

Phenylacetyl chloride, $C_6H_5.CH_2.COCl$, was obtained by Strecker and Möller from the acid by the action of phosphorus pentachloride, while Popow prepared it from the calcium salt and phosphorus oxychloride.[5] It is a colourless, fuming liquid, which decomposes very readily, especially on distillation,[6] and has therefore not yet been prepared pure.

Phenylacetamide, $C_6H_5.CH_2.CO.NH_2$, is formed by the action of ammonia on the chloride (Strecker and Möller). It is also obtained when the ethyl ether is heated with ammonia to

[1] Radziszewski, *Ber. Deutsch. Chem. Ges.* ii. 207.
[2] Hodgkinson, *Journ. Chem. Soc.* 1880, i. 480.
[3] Hauff, *Ber. Deutsch. Chem. Ges.* xx. 592.
[4] *Journ. Chem. Soc.* 1880, i. 480; Slawik, *Ber. Deutsch. Chem. Ges.* vii. 1051.
[5] *Ibid.* v. 550.
[6] Hofmann, *ibid.* xiii. 1234.

140°-150° [1] and by heating the nitril with an alcoholic solution of potassium hydrosulphide.[2] It crystallizes in small plates which have a satin-lustre, or thin tablets which are slightly soluble in cold, readily in hot water and alcohol, and melt at 154°–155°.

Phenylaceturic acid, $C_6H_5.CH_2.CO.NH.CH_2.CO_2H$, was detected by E. and H. Salkowski in the urine of dogs, to which 1·5–2 grms. of phenylacetic acid, generally combined with soda, were administered daily with their food.[3] E. Salkowski then discovered that it is a normal constituent of the urine of the horse,[4] and Hotter obtained it by the action of phenylacetyl chloride on an alkaline solution of amidoacetic acid.[5] It crystallizes from hot water in aggregates of thin plates, or in compact pointed prisms, melting at 143°. On boiling with hydrochloric acid, it decomposes into phenylacetic acid and amidoacetic acid.

2281 *Phenylacetonitril*, $C_6H_5.CH_2.CN$, was first prepared, as already mentioned, by Cannizzaro, who named it *benzyl cyanide*, by heating an alcoholic solution of benzyl chloride with potassium cyanide. He did not however investigate its properties more fully, but converted it into phenylacetic acid; Radziszewski subsequently prepared it pure by the same reaction.[6] Tribenzylamine [7] and phenylacetamide [8] have been noticed as bye-products in its preparation. Barbaglia then showed that it is also formed by the distillation of potassium benzylsulphonate with potassium cyanide.[9] The occurrence of this nitril in nature is especially interesting; Hofmann found that it forms the chief constituent of the ethereal oils of the garden nasturtium (*Tropaeolum majus*) and common cress (*Lepidium sativum*).[10]

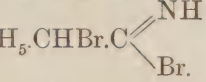
It is prepared by Mann's method, which is described under phenylacetic acid, the product being freed from alcohol, distilled with steam, dried and rectified. It is a colourless liquid which has a faint but characteristic odour and boils at 232°.

Phenylbromacetimido-bromide, $C_8H_7Br_2N$, is formed, together

[1] *Ber. Deutsch. Chem. Ges.* viii. 692; Bernthsen, *Ann. Chem. Pharm.* clxxxiv. 294, 316.
[2] Weddige, *Journ. Prakt. Chem.* [2] vii. 99.
[3] *Ber. Deutsch. Chem. Ges.* xii. 653.
[4] *Ibid.* xvii. 3010.
[5] *Ibid.* xx. 81.
[6] *Ber. Deutsch. Chem. Ges.* iii. 198.
[7] Frankland and Tompkins, *Journ. Chem. Soc.* 1880, i. 566.
[8] *Ber. Deutsch. Chem. Ges.* xiii. 741.
[9] *Ibid.* v. 270.
[10] *Ibid.* vii. 518 and 1293.

with phenylbromacetonitril, by heating phenylacetonitril with bromine. The oily product, which has a very disagreeable odour, a pungent taste, and a vapour which violently attacks the eyes, deposits crystals of the compound on standing, more rapidly on the addition of a large quantity of ether. It is formed according to the following equation:

$$C_6H_5.CH_2.CN + Br_2 = C_6H_5.CHBr.CN + HBr =$$



It is only very slightly soluble in all solvents, most readily in boiling glacial acetic acid. On heating to 150° with dilute hydrochloric acid it is converted into phenylhydroxyacetic acid, $C_6H_5.CH(OH)CO_2H$.[1]

Cyanbenzine, $C_{24}H_{21}N_3$, is formed in small quantity, together with other products, by the action of zinc ethyl on phenylacetonitril, and crystallizes from hot alcohol in fascicular aggregates of needles, which melt at 170°–171°.

Benzacin, $C_{32}H_{27}N_2O$, is a product of the same reaction as the preceding compound; it is more readily soluble in alcohol and crystallizes in rhombohedral or hexagonal tablets, melting at 150° (Frankland and Tompkins).

HALOGEN SUBSTITUTION PRODUCTS OF PHENYLACETIC ACID.

2282 These derivatives may be divided into two groups, since the substitution may be effected either in the nucleus or in the side-chain. In the first case, para-compounds form the chief product, ortho-compounds being also formed, while benzoic acid yields meta-substitution products.

Parachlorophenylacetic acid, $C_6H_4Cl.CH_2.CO_2H$. The oily nitril of this acid is obtained by heating parachlorobenzyl chloride or bromide with alcohol and potassium cyanide,[2] and the free acid is formed when phenylacetic acid is treated with chlorine in the sunlight.[3] It crystallizes from hot water in fine needles, which melt at 104° (Jackson and Field).

[1] Reimer, *Ber. Deutsch. Chem. Ges.* xiv. 1797.
[2] Neuhof, *Ann. Chem. Pharm.* cxlvii. 347; Jackson and Field, *Ber. Deutsch. Chem. Ges.* xi. 905.
[3] Radziszewski, *ibid.* ii. 207.

Parabromophenylacetic acid, $C_6H_4Br.CH_2.CO_2H$, is formed, together with the ortho-acid, by the bromination of phenylacetic acid,[1] and by heating the corresponding nitril to 100° with hydrochloric acid.[2] It is most conveniently prepared by adding bromine in small quantities to a well cooled mixture of phenylacetic acid, mercuric oxide, and water. The mercury is then removed with caustic soda, the brominated acids precipitated in the filtrate with hydrochloric acid and separated by means of their barium salts, that of the para-acid being the less soluble.[3] Parabromophenylacetic acid crystallizes from hot water in long, flat needles, resembling those of benzoic acid, which melt at 114°-115°.

Parabromophenylacetonitril, $C_6H_4Br.CH_2.CN$, is obtained from parabromobenzylbromide and potassium cyanide, and crystallizes in truncated quadratic pyramids, resembling those of potassium ferrocyanide, or forms twin crystals, which have a similar appearance to the conventional architectural form of the four-leaved clover. It melts at 46° and has a strong, unpleasant odour.

Orthobromophenylacetic acid crystallizes from hot water in flat, lustrous needles, and from glacial acetic acid on gradual evaporation in well-developed monosymmetric prisms, melting at 103°-104°. Its nitril is an oily liquid, which does not solidify in a freezing mixture.[4]

Para-iodophenylbenzoic acid, $C_6H_4I.CH_2.CO_2H$. The nitril of this acid, which is prepared from para-iodobenzyl bromide, crystallizes in nacreous tablets, which have a characteristic odour and melt at 50·5°. On heating with hydrochloric acid to 100°, it yields the acid, which crystallizes from hot water in pointed tablets, which melt at 135° and possess a pleasant odour.[5]

NITROPHENYLACETIC ACIDS.

2283 Radziszewski found that the products of nitration of phenylacetic acid consist chiefly of the para-compound, together with a smaller quantity of the orthonitro-acid.[6] He did not,

[1] Radziszewski, *loc. cit.*
[2] Jackson and Lowery, *Ber. Deutsch. Chem. Ges.* x. 1209.
[3] Bedson, *Journ. Chem. Soc.* 1880, i. 94.
[4] Jackson and White, *Ber. Deutsch. Chem. Ges.* xiii. 1219.
[5] Jackson and Mabery, *Ber. Deutsch. Chem. Ges.* xi. 55.
[6] *Ibid.* ii. 209 ; iii. 648.

however, obtain the pure compounds, since, according to Maxwell, these crystallize together and form mixtures with a constant melting point, in the same way as the nitrobenzoic acids. The latter chemist succeeded in preparing the methyl ether of the para-compound in the pure state, and from it the acid.[1] Radziszewski also found that the barium salt of the para-acid is less soluble than that of the ortho-derivative. A complete separation cannot be effected in this way, but the acids precipitated from the resulting purified salts can be obtained pure by recrystallization:[2]

Paranitrophenylacetic acid, $C_6H_4(NO_2)CH_2.CO_2H$. In order to prepare this substance, 2 parts of phenylacetic acid are dissolved in 20 parts of fuming nitric acid, the solution poured into 4 volumes of water and allowed to evaporate slowly on the water-bath. An impure paranitrophenylacetic acid, melting at 114°, crystallizes out on cooling; this is dissolved in 3 volumes of methyl alcohol and the solution saturated with hydrochloric acid gas. After a few hours the liquid is heated to drive off the excess of methyl alcohol and hydrochloric acid, agitated with sodium carbonate solution, and extracted with ether; the methyl paranitrophenylacetate crystallizes from the oily residue left on the evaporation of the ethereal solution, and is purified by recrystallization from petroleum spirit. The pure compound is neutralized with caustic soda, and the free acid precipitated with hydrochloric acid (Maxwell). Bedson obtained the pure acid by repeatedly recrystallizing the acid prepared from the slightly soluble barium salt from hot, dilute alcohol. According to Gabriel, it is best obtained by heating its nitril to 100° for several hours with an excess of hydrochloric acid.[3] It crystallizes from hot water in long, yellowish, brittle needles, melting at 151°-152°. Chromic acid solution oxidizes it to paranitrobenzoic acid.

Barium paranitrophenylacetate, $(C_6H_4(NO_2)CH_2.CO_2)_2Ba + 7H_2O$, crystallizes from a slowly cooled solution in transparent, light yellow, six-sided tablets, which become opaque and effloresce in the air.

Methyl paranitrophenylacetate, $C_6H_4(NO_2)CH_2.CO_2.CH_3$, crystallizes from alcohol in yellowish tablets, and from petroleum-spirit in lustrous needles, two or three inches in length, which melt at 54°.

[1] Jackson and Mabery, *Ber. Deutsch. Chem. Ges.* xii. 1764.
[2] Bedson, *Journ. Chem. Soc.* 1880, i. xc.
[3] *Ber. Deutsch. Chem. Ges.* xiv. 2341.

Ethyl paranitrophenylacetate, $C_6H_4(NO_2)CH_2.CO_2.C_2H_5$, was obtained by Maxwell in a similar manner to the methyl ether, while Radziszewski prepared it by the nitration of ethyl phenylacetate. It crystallizes from petroleum-spirit in broad, thin tablets, melting at 65·5°-66°.

These ethers are coloured a fine violet by caustic potash in alcoholic solution.

Paranitrophenylacetonitril, $C_6H_4(NO_2)CH_2.CN$, is obtained when one part of phenylacetonitril is brought into nine parts of fuming nitric acid and the solution precipitated with water; it crystallizes from boiling alcohol in colourless, compact needles, melting at 116° (Gabriel). Small quantities of the ortho- and meta-compounds are simultaneously formed (Salkowski).

Orthonitrophenylacetic acid. When the mixture of nitro-acids is crystallized from alcohol and the mother liquors concentrated, or when the more readily soluble barium salt is decomposed with hydrochloric acid, an acid is obtained which crystallizes in fascicular needles and melts at 112°-117°. If this be dissolved in wood-spirit or ordinary alcohol and the solution allowed to evaporate spontaneously, the ortho-compound is deposited in large crystals, which are then purified by recrystallization. It forms needles or monosymmetric tablets, which melt at 141° (Salkowski), and are oxidized to orthonitrobenzoic acid by potassium permanganate.

Barium orthonitrophenylacetate, $(C_6H_4(NO_2)CH_2\,CO_2)_2Ba + 2H_2O$, crystallizes in white, lustrous scales.

Orthonitrophenylacetonitril separates from solution in glacial acetic acid in large, well-formed rhombic prisms, which melt at 84° and are readily converted into the acid by heating with hydrochloric acid (Salkowski). The nitril may also be obtained by heating an alcoholic solution of orthonitrobenzyl chloride with potassium cyanide. A larger quantity of *dinitrocyandibenzyl*, $C_6H_4(NO_2)CH(CN)CH_2.C_6H_4NO_2$, is always simultaneously formed; this substance may also be prepared by heating orthonitrobenzyl chloride with orthnitrophenylacetonitril, and crystallizes in short, thick prisms, which melt at 110·5°.[1]

Metanitrophenylacetic acid was prepared by Gabriel and Borgmann from its nitril;[2] it crystallizes from hot water in long thin needles, melting at 120° (Salkowski).

[1] Bamberger, *Ber Deutsch. Chem. Ges.* xix. 2635.
[2] *Ibid.* xvi. 2064; Borgmann, *Chem. Centralbl.* 1855, 456.

Metanitrophenylacetonitril forms large, well-developed monosymmetric crystals, melting at 61°.[1]

Dinitrophenylacetic acid, $C_6H_3(NO_2)_2CH_2.CO_2H$ (4 : 2 : 1), was obtained by Radziszewski by the action of a mixture of sulphuric and nitric acids on paranitrophenylacetic acid. In order to prepare it, 50 grms. of phenylacetic acid are added in small quantities to 300 grms. of red fuming nitric acid, 500 grms. of sulphuric acid being then added and the mixture poured into ten volumes of cold water after standing for ten minutes.[2] It crystallizes from hot water in fine yellowish needles, which melt at 160° and decompose at a higher temperature into carbon dioxide and ordinary dinitrotoluene. The alkali salts of the acid undergo this decomposition in aqueous solution at the ordinary temperature and instantaneously on boiling :

$$C_6H_3(NO_2)_2CH_2.CO_2K + H_2O = C_6H_3(NO_2)_2CH_3 + CO_3KH.$$

Bergmann obtained two nitro-acids by the further nitration of metanitrophenylacetic acid, one of which is soluble in benzene and melts at 137°, while the other is insoluble and melts at 152°.

AMIDOPHENYLACETIC ACIDS.

2284 *Paramidophenylacetic acid*, $C_6H_4(NH_2)CH_2.CO_2H$, is obtained by the reduction of paranitrophenylacetic acid with tin and hydrochloric acid. It crystallizes from hot water in white iridescent plates, which become coloured brown in the air and melt with decomposition at 199°—200°, (Bedson).

Paramidophenylacetonitril, $C_6H_4(NH_2)CH_2.CN$, has been prepared by the reduction of paranitrophenylacetonitril; it crystallizes from hot water in broad plates, which melt at 43·5° – 44·5°.[3]

Orthonitroparamidophenylacetic acid, $C_6H_3(NH_2)(NO_2)CH_2.CO_2H$, (4 : 2 : 1) is formed by the reduction of the dinitro-acid by means of aqueous ammonium sulphide and crystallizes from hot water in long, broad, yellowish red to reddish brown needles,

[1] Salkowski, *Ber. Deutsch. Chem. Ges.* xvii. 504.
[2] Meyer and Gabriel, *ibid.* xiv., 823.
[3] Czumpelik, *ibid.* iii. 474 ; Gabriel, *ibid.* xv. 835.

which melt at 184°—186°. The following reaction takes place when it is subjected to the action of amyl nitrite and an excess of hydrochloric acid:

$$NH_2.C_6H_3(NO_2)CH_2.CO_2H + 2NO_2H + HCl =$$
$$ClN{=}NC_6H_3(NO_2)C{=}N.OH + CO_2 + 3H_2O.$$

The diazo-compound obtained in this way forms long, lustrous, pale red needles, and decomposes on heating with alcohol with formation of orthonitrobenzaldoxime (Part IV. page 146). The ethyl ether, which is prepared by the action of hydrochloric acid on the alcoholic solution of the acid, crystallizes in long, fine, yellow needles, which melt at 100°. When it is brought into a heated mixture of concentrated hydrochloric acid and ethyl nitrate, *ethyl isonitrosonitrophenylacetate* is formed; this substance crystallizes from hot water in long yellowish needles, which melt at 163° and decompose on heating with formation of orthonitrobenzoic acid.[1]

$$C_6H_4(NO_2)C(NOH)CO_2.C_2H_5 + 2HCl + H_2O =$$
$$C_6H_4(NO_2)CO_2H + C_2H_5Cl + CO_2 + NH_4Cl.$$

The same compound is formed by the action of hydroxylamine on ethyl orthonitrobenzoyl formate,[2] $C_6H_4(NO_2)CO.CO_2.C_2H_5$.

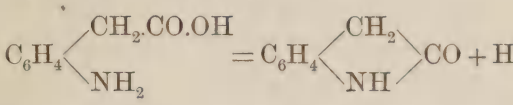
Metanitroparamidophenylacetic acid, $C_6H_3(NH_2)(NO_2).CH_2.CO_2H$ (4:3:1), is prepared by heating paramidophenylacetonitril with acetic anhydride and treating the product with concentrated nitric acid, the acetyl-derivative *metanitroacetamidophenylacetonitril*, $C_6H_3(NO_2)NH(C_2H_3O)CH_2CN$, being thus formed. It crystallizes in sulphur-yellow, flat needles or plates, which melt at 112°—113° and yield the nitro-amido-acid on boiling with concentrated hydrochloric acid. This substance crystallizes from hot water in broad orange-yellow tablets or pointed needles and melts at 143·5°—144·5°. It also yields a diazo-compound which crystallizes in light red, rectangular tablets or pointed needles and is converted into metanitrobenzaldoxime by heating with alcohol.[3]

Metamidophenylacetic acid, $C_6H_4(NH_2)CH_2.CO_2H$, crystallizes from hot water in small, yellowish tablets, which melt at 148°—149° (Gabriel and Borgmann).

[1] Gabriel and Meyer, *Ber. Deutsch. Chem. Ges.* xiv. 823: Meyer. *Chem. Centralbl.* 1855, 516.
[2] Gabriel, *Ber. Deutsch. Chem. Ges.* xvi. 571.
[3] *Ibid.* xv. 843.

Metamidophenylacetonitril, $C_6H_4(NH_2)CH_2.CN$, is an oily liquid, which does not solidify at $-17°$ (Salkowski).

Ortho-amidophenylacetic acid is not known to exist in the free state, since, like other ortho-compounds, it immediately loses water and passes into the anhydride:



Oxindol, as this substance has been named, was first prepared by Baeyer and Knop[1] by the reduction of *isatin* $C_8H_5NO_2$, an oxidation product of indigo, which will be subsequently described. Baeyer,[2] and also Bedson[3] then succeeded in obtaining it by the reduction of orthonitrophenylacetic acid.

In order to prepare it from isatin, this is suspended in water to which 5 per cent. sodium amalgam is gradually added, the temperature not being allowed to rise. The liquid first becomes coloured dark violet, then brown and finally a dirty yellow, *dioxindol*, $C_8H_7NO_2$, which cannot be further reduced in alkaline solution, being formed. The solution is then diluted with water until 100 parts of this are present for every part of isatin employed, this degree of dilution being necessary to prevent the formation of condensation products. It is then acidified with hydrochloric or sulphuric acid, heated in bath of boiling water and again treated with sodium amalgam, the liquid being kept acid throughout the operation. When the solution retains its light yellow colour even when rendered alkaline, it is neutralized with sodium carbonate and evaporated until oily drops are formed on the surface. The oxindol separates on cooling in long, yellow, strongly refractive needles, an additional quantity of which can be obtained by concentration.

It may be more easily prepared from orthonitrophenylacetic acid, which need not be pure. This is reduced in the cold with tin and hydrochloric acid, the tin precipitated with sulphuretted hydrogen and the filtrate boiled with calcium carbonate. The oxindol is then removed from the solution by ether, while calcium paramidophenylacetate remains behind. After repeated crystallization from hot water the oxindol forms long, colourless needles or feathery groups; it melts at 120°, and distils without decomposition when a small quantity is heated.

[1] *Ann. Chem. Pharm.* cxl. 1. [2] *Ber. Deutsch. Chem. Ges.* xi. 583.
[3] *Journ. Chem. Soc.* 1880, i. 93.

Oxindol silver, C_8H_6AgNO, is obtained by the careful addition of ammonia to a solution of oxindol and silver nitrate, in the form of a flocculent precipitate which becomes granular on standing.

Oxindol hydrochloride, $C_8H_7NO.HCl$, forms pointed crystals which are readily soluble in water.

Ethyloxindol, $C_8H_6(C_2H_5)NO$, is formed by heating an alcoholic solution of oxindol with sodium ethylate and ethyl iodide. It is an oily, faintly smelling liquid, which is not decomposed when heated with baryta water or hydrochloric acid.[1]

Acetoxindol, $C_8H_6(C_2H_3O)NO$, is obtained by boiling oxindol with acetic anhydride, and crystallizes from hot water in long needles, melting at 126°. When it is dissolved in cold caustic soda, and the solution acidified with sulphuric acid, *acetortho-amidophenylacetic acid* is precipitated :

$$C_6H_4\begin{cases}CH_2\\ >CO\\ N.CO.CH_3\end{cases} + H_2O = C_6H_4\begin{cases}CH_2.CO.OH\\ \\ NH(CO.CH_3).\end{cases}$$

This body, which has not yet been obtained perfectly pure, forms a crystalline mass, which is again converted into oxindol by heating with caustic soda or hydrochloric acid.[2]

Nitro-oxindol, $C_8H_6(NO_2)NO$, was prepared by Baeyer by the addition of saltpetre to a solution of oxindol in sulphuric acid. It crystallizes from hot water in yellow needles or granules, which decompose at 175°.[3]

Paramido-oxindol, $C_8H_6(NH_2)NO$, is formed by the action of tin and hydrochloric acid on dinitrophenylacetic acid :

$$C_6H_3(NO_2)\begin{cases}NO_2\\ \\ CH_2.CO.OH\end{cases} + 12H = C_6H_3(NH_2)\begin{cases}NH\\ \\ CH_2\end{cases}CO + 5H_2O.$$

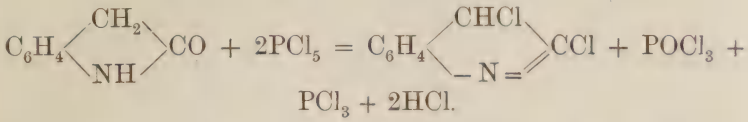
It crystallizes from hot water in long needles, which have a vitreous lustre and become dark-coloured in the air. It combines with acids to form salts, which crystallize well.[4]

A compound isomeric with this has been prepared from oxindol, which is converted by nitrous acid into a compound

[1] Baeyer and Comstock, *Ber. Deutsch. Chem. Ges.* xvi. 1704.
[2] Suida, *Ber. Deutsch. Chem. Ges.* xii. 1236.
[3] *Ibid.* xii. 1313.
[4] Gabriel and Meyer, *ibid.* xiv. 832.

which was formerly thought to be nitroso-oxindol, but was subsequently recognised as isatinoxime, and is converted by reduction into the isomeric amido-oxindol, which will therefore be described under isatin.

Chloroxindol chloride, $C_8H_5Cl_2N$, is the product of the action of phosphorus pentachloride on oxindol:



$$C_6H_4\left\langle\begin{matrix}CH_2\\NH\end{matrix}\right\rangle CO + 2PCl_5 = C_6H_4\left\langle\begin{matrix}CHCl\\-N=\end{matrix}\right\rangle CCl + POCl_3 + PCl_3 + 2HCl.$$

It crystallizes from hot water in lustrous plates, which are readily soluble in alcohol and ether, and melt at 103°—104°. It has a characteristic pungent, fæcal odour, and is volatile with steam. It dissolves in caustic potash without change, and is not attacked by sodium amalgam either in acid or alkaline solution, while it is converted into indol, C_8H_7N, on heating with zinc dust.

Retindol is formed when the chloride is brought into glacial acetic acid saturated with hydriodic acid. It is precipitated by water in white amorphous flocks, and is converted into indol by dry distillation, a portion being, however, carbonized.[1]

HYDROXYPHENYLACETIC ACIDS, $C_6H_4(OH)CH_2.CO_2H$.

2285 *Parahydroxyphenylacetic acid* was discovered by E. and H. Salkowski in the products of the putrefaction of wool,[2] and was afterwards detected by Baumann in human urine,[3] and by Brieger in a putrid, pleuritic exsudation.[4] H. Salkowski then prepared it by the action of nitrous acid on paramidophenylacetic acid,[5] and, in conjunction with his brother, detected it among the putrefaction products of albumen.[6] It may also be obtained by the action of hydrochloric acid or caustic soda on its nitril.

[1] Baeyer, *Ber. Deutsch. Chem. Ges.* xii. 457.
[2] *Ber. Deutsch. Chem. Ges.* xii. 648.
[3] *Ibid.* xiii. 279.
[4] *Zeitschr. phyzikal. Chem.* v. 367.
[5] *Ber. Deutsch. Chem. Ges.* xii. 1438.
[6] *Ibid.* xiii. 189.

It is tolerably soluble in cold, readily in hot water, and crystallizes in very brittle prismatic needles, which melt at 148°, and sublime to a small extent without decomposition, a portion of the residue being always decomposed. Its aqueous solution is coloured greyish-violet by ferric chloride, but this soon passes into a dirty greyish-green. On distillation with lime it yields paracresol.

Parahydroxyphenylacetonitril, $C_6H_4(OH)CH_2.CN$, was first obtained from sinalbin (Part IV. page 377), by Laubenheimer and Will, and was then prepared by H. Salkowski by the action of nitrous acid on paramidophenylacetonitril.[1] It crystallizes in large, lustrous, monosymmetric tablets, which melt at 69°—70°, are slightly soluble in cold, readily in hot water, and give a violet colouration with ferric chloride.

Methylparahydroxyphenylacetic acid, $C_6H_4(OCH_3)CH_2.CO_2H$, was first prepared by Cannizzaro, who heated anisyl chloride (Part IV. page 332) with potassium cyanide and alcohol, and then decomposed the nitril thus obtained with caustic potash. It crystallizes from hot water in nacreous plates melting at 85°—86°.[2]

Methylparahydroxyphenylacetonitril, $C_6H_4(OCH_3)CH_2.CN$, is also formed when parahydroxyphenylacetonitril is heated with caustic potash and methyl iodide. It is a liquid which readily yields the acid on heating with hydrochloric acid (Salkowski).

Metahydroxyphenylacetic acid has been prepared from its nitril and from metamidophenylacetic acid. It is so soluble in water that it can only be removed from solution by evaporation to dryness. It crystallizes from a hot mixture of petroleum spirit and benzene in fine needles, more compact crystals being formed when the solution is more gradually cooled. It melts at 129°, and yields a fugitive violet colouration with ferric chloride.

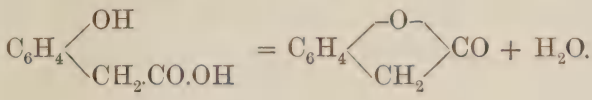
Metahydroxyphenylacetonitril is readily soluble in hot water, from which it separates as an oily liquid, which solidifies on standing in contact with the solid compound. The latter is obtained in rhombic tablets, melting at 52°—53°, by the gradual evaporation of the solution. Ferric chloride gives a beautiful violet colouration.[3]

Orthohydroxyphenylacetic acid has been prepared by Baeyer and Fritsch by the reduction of orthohydroxymandelic acid, $C_6H_4(OH)CH(OH)CO_2H$, with hydriodic acid. It crystallizes in

[1] *Ber. Deutsch. Chem. Ges.* xvii. 504.
[2] *Ann. Chem. Pharm.* cxvii. 246.
[3] H. Salkowski, *Ber. Deutsch. Chem. Ges.* xvii. 506.

needles, which melt at 137°, are tolerably soluble in water, and give the same colouration as salicylic acid, with ferric chloride.

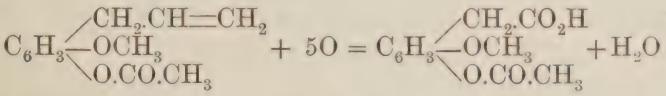
On distillation it is resolved into water and its lactone, which corresponds to oxindol:



It is readily soluble in hot water, crystallizes from ether in large rhomboid tablets, melts at 490°, and boils at 236°—238°. It is gradually converted into the acid by water, rapidly by alkalis.[1]

DIHYDROXYPHENYLACETIC ACIDS, $C_6H_3(OH)_2CH_2.CO_2H$.

2286 *Alphahomoprotocatechuic acid* ($CH_2 : OH : OH = 1 : 3 : 4$). —When aceteugenol is treated in acetic acid solution with potassium permanganate, acetylalphahomovanillic acid is formed, together with acetylvanillin and acetylvanillic acid:



On heating with caustic soda it is converted into alphahomovanillic acid, which yields methyl chloride and alphahomoprotocatechuic acid on heating with hydrochloric acid to 170°—180°. This is extremely soluble in water and alcohol, but almost insoluble in cold, and only slightly in hot benzene, from which it crystallizes in fine, lustrous, transparent needles, melting at 127°. Ferric chloride produces a grass-green colouration in the aqueous solution; this colour changes through dark green and blue to a reddish violet on the gradual addition of sodium carbonate solution or ammonia. It is a strong acid, and forms well-defined salts; like protocatechuic acid, it reduces Fehling's solution and ammoniacal silver nitrate solution. On fusion with potash it yields protocatechuic acid.

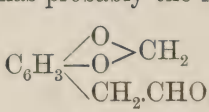
Alphahomovanillic acid, $C_6H_3(OCH_3)(OH)CH_2.CO_2H$, is slightly

[1] H. Salkowski, *Ber. Deutsch. Chem. Ges.* xvii. 973.

soluble in cold, readily in hot water and alcohol, and crystallizes in transparent, six-sided prisms, which melt at 142°—143°.[1]

Alphahomoveratric acid, $C_6H_3(OCH_3)_2CH_2.CO_2H$, is formed when the preceding compound is heated with caustic potash and ethyl iodide, and crystallizes from water in fine white needles, containing water of crystallization which is gradually lost over sulphuric acid. The anhydrous acid melts at 98°—99°.[2]

Paracoumarhydrin, $C_9H_8O_3$. This substance, which is metameric with coumaric acid, $C_6H_4(OH)C_2H_2.CO_2H$, is formed when paracoteïn, $C_{19}H_{12}O_6$, is heated with caustic potash, and crystallizes in plates, which smell like coumarin, and melt at 82°—83°. An acid, which probably has the formula $C_9H_8O_4$, is also formed in the reaction; it is very similar to the piperonylic acid which occurs with paracoteïn in the Paracoto-bark (Part IV. p. 355).[3] Paracoumarhydrin appears therefore to be homologous with piperonal, and, since paracoteïn yields protocatechuic acid on fusion with potash, has probably the following constitution:



STYROELNE, ETHENYLBENZENE, OR PHENYLETHYLENE, $C_6H_5.CH{=}CH_2$.

2287 Bonastre, by the distillation of liquid styrax[4] with water, obtained a volatile oil, which was more closely investigated by Simon, who decided that it was a hydrocarbon isomeric with

[1] Tiemann and Nagai, *Ber. Deutsch. Chem. Ges.* x. 201.
[2] Tiemann and Matsmoto, *ibid.* xi. 143; Nagai, *ibid.* xi. 658.
[3] Jobst and Hesse, *Ann. Chem. Pharm.* cxcix. 30.
[4] Liquid styrax (*styrax liquidus*) is mentioned at a very early date by the Grecian and Arabian physicians, and was exported by the Arabs to India and China, which still receive the larger portion of the annual production. Its origin was very doubtful, and it has only recently been ascertained with certainty that it is derived from *Liquidambar orientalis*, a tree which forms forests in the south-west of Asia Minor. In order to obtain the balsam the exterior bark is removed, and the interior cut off with a specially constructed knife, and boiled in copper vessels with sea water. The resinous sap is thus separated, and can be skimmed off the liquid, a further quantity being obtainable by pressing the boiled bark (Flückiger and Hanbury, *Pharmacographia*, 2nd ed. p. 271).

Liquid styrax contains styrolene, cinnamic acid, cinnamyl cinnamate, $C_6H_5.C_2H_2.CO_2.C_3H_4.C_6H_5$, phenylpropyl cinnamate, $C_6H_5.C_2H_2.CO_2.C_3H_6.C_6H_5$, some ethyl cinnamate, and a small quantity of a pleasant-smelling substance, which is probably ethylvanillin. The chief constituent, however, is the resinous storesin, $C_{36}H_{55}(OH)_3$, and its cinnamic ether (Miller, *Ann. Chem. Pharm.* clxxxviii. 184; clxxxix. 338).

benzene, and named it *styrol*. By the distillation of cinnamic acid with slacked lime, he obtained another hydrocarbon, also isomeric with benzene, but different from styrol, and gave it the name of *cinnamomin*.[1] This substance was prepared in a similar manner by Herzog, and named *cinnamol*.[2] Mitscherlich, however, showed that the body obtained in this way is not a single compound, but a mixture of hydrocarbons, among which benzene is present.[3] Gerhardt and Cahours, on the other hand, found that when cinnamic acid is distilled with four times its weight of baryta, a hydrocarbon with constant boiling-point is formed. They determined the composition and vapour density of this substance, and named it *cinnamene* (*cinnamène*).[4] According to E. Kopp, this body is identical with styrol, since it behaves chemically in a similar manner, and does not differ from it more than the different kinds of turpentine from one another.[5] Blyth and Hofmann confirmed the results of Mitscherlich and Gerhardt and Cahours, and showed in addition that, as Simon had previously observed, styrol is converted on heating into a solid body, which, however, preserves its original composition, and was therefore named *metastyrol*. They prepared a number of derivatives of styrol, all of which pointed to C_8H_8 as its formula; they observed, however, that when it and cinnamene, or, as they termed it, cinnamol, were heated in sealed tubes to 200° for half an hour, the styrol solidified completely, while the cinnamol lost none of its mobility. They remark on this point:—"This research appears at the first glance to decisively negative the opinion that styrol and cinnamol are identical. If, however, it be borne in mind that the product obtained by distillation with lime certainly contained other compounds in addition to cinnamol, while that prepared by the action of baryta could not, on account of its small quantity, be examined in this respect, we must conclude that a definite answer to this question can only be given by future investigations."[6] Hempel now found that a hydrocarbon which behaves in a precisely similar manner to styrol is formed when the vapour of cinnamic acid is passed through a red-hot tube, as well as by the distillation of copper cinnamate,[7] and also by the slow distillation of free cinnamic acid, $C_6H_5.CH{=}CH.CO_2H$.[8]

[1] *Ann. Chem. Pharm.* xxxi. 265.
[2] *Ibid.* liii. 323.
[3] *Ibid.* liii. 321.
[4] *Ann. Chim. Phys.* [3], i. 96.
[5] *Compt. Rend.* xxi. 1376.
[6] *Ann. Chem. Pharm.* liii. 289.
[7] *Ibid.* lix. 316.
[8] Miller, *ibid.* clxxxix. 338.

Berthelot, on the other hand, observed that cinnamol is optically inactive, while styrol is lævo-rotatory.[1] This appeared remarkable, inasmuch as it does not contain an asymmetric carbon atom, and van't Hoff proved that the hydrocarbon obtained from styrax contains varying quantities of an impurity, to which it owes its rotatory power.[2]

Styrol or cinnamol is phenylethylene, and is thus best named styrolene. It has been prepared by a number of different reactions in addition to the methods already mentioned.

Glénard and Boudault obtained by the dry distillation of dragon's blood, dracyl, which was subsequently recognized as toluene (Part III. page 60) and *draconyl*, which, according to Hofmann and Blyth, is identical with metastyrol. Bötsch found that, when dragon's blood is distilled with zinc dust, 66 per cent. of styrolene are formed, in addition to ethylbenzene, a little toluene, and a smaller quantity of higher boiling substance.[3]

Berthelot obtained it, together with benzene and other hydrocarbons, by heating acetylene to the softening point of glass,[4] and by passing a mixture of ethylene and benzene through a red-hot tube ;[5] he also discovered it in coal-tar.[6] Thorpe found that it is also formed when secondary styrolyl bromide, $C_6H_5.CHBr.CH_3$ is distilled or heated with alcohol potash (Part V. page 9).

It was formerly prepared by the distillation of liquid styrax with water, to which sodium carbonate was added to prevent any cinnamic acid passing over (Simon). It is now obtained by the slow distillation of cinnamic acid, which is manufactured on the large scale. When cinnamic acid is allowed to stand for some days in contact with the most concentrated hydrobromic acid, phenylbromopropionic acid, $C_6H_5.CHBr.CH_2.CO_2.H$, is formed, and this is decomposed by sodium carbonate solution with formation of styrolene. A still better yield is obtained when phenyliodopropionic acid, which is prepared in a similar manner, is boiled with sodium carbonate solution.[7]

Properties—Styrolene is a strongly refractive liquid, which has an aromatic odour, boils at 144°·5 and has a sp. gr. of 0·925 at 0°. It yields benzoic acid on oxidation (Blyth and Hofmann).

[1] Miller, *Ann. Chem. Pharm.* cxli. 378.
[2] *Ber. Deutsch. Chem. Ges.* ix. 5 and 1339 ; Krakau, *ibid.* xi. 1260.
[3] *Monatshefte f. Chem.* i. 609.
[4] *Ann. Chem. Pharm.* cxli. 181.
[5] *Ibid.* cxlii. 257.
[6] *Ibid.* Suppl. iii. 368.
[7] Fittig and Binder, *ibid.* cxcv. 137.

Metastyrolene. This polymeric modification is gradually formed when pure styrolene is allowed to stand, more rapidly at 200°, or when it is treated with concentrated sulphuric acid.[1] It is a vitreous mass, which is strongly refractive, and is converted on distillation into styrolene.

Polystyrolene, $(C_8H_8)_n$ is formed, together with other products, by the dry distillation of calcium cinnamate,[2] by passing styrolene dibromide over heated lime,[3] and, together with styrolene, by the gradual distillation of cinnamic acid (Müller). It crystallizes from ether or alcohol in tablets, melting at 119°.

Distyrolene, $C_{16}H_{16}$, was obtained by Erlenmeyer by heating cinnamic acid to 150°—240° with hydrobromic acid; he found that hydrochloric and dilute sulphuric acids have the same action, and that it is also formed by heating styrolene with hydrochloric acid to 170°.[4] Fittig prepared it, together with distyrolenic acid, $C_{17}H_{16}O_2$, by boiling cinnamic acid with sulphuric acid, which was diluted with one or one and a half volumes of water.[5] It is a liquid, which boils at 310°—312°, yields benzoic acid on oxidation, and combines with bromine to form *distyrolene bromide,* $C_{16}H_{16}Br_2$, which crystallizes in loose masses of needles. When distyrolene is kept for some time at the boiling-point, it decomposes with formation of toluene, styrolene, isopropylbenzene, and other high-boiling hydrocarbons. It is probably a *diphenylbutylene* of the following constitution (Fittig):

$$C_6H_5.CH{=}CH.CH\begin{matrix}CH_3\\C_6H_5\end{matrix}.$$

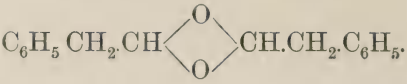
Styrolene forms substitution products, and also, as an olefine, addition products.

2288 *Styrolene alcohol,* $C_6H_5.CH(OH)CH_2.OH$. This compound, which is also known as *phenylglycol,* is most easily prepared by boiling styrolene bromide for three or four days with one molecule of potassium carbonate, dissolved in four parts of water; the monobromostyrolene, which is simultaneously formed, is then distilled off, and the glycol extracted from the residue with ether. On evaporation it is left as an oil, which gradually crystallizes. It is readily soluble in water,

[1] Berthelot, *Bull. Soc. Chim.* vi. 296.
[2] Engler and Leist, *Ber. Deutsch. Chem. Ges.* vi. 254.
[3] Radziszewski, *ibid.* vi. 492.
[4] *Ann. Chem. Pharm.* cxxxv. 122.
[5] *Ibid.* ccxvi. 187.

alcohol, ether, &c., and is best crystallized from a hot mixture of benzene and petroleum spirit, from which it separates on cooling in fine silky needles, melting at 67°—68°.

Styrolene alcohol boils at 272°—274°, and is converted by boiling with dilute sulphuric acid into phenylacetaldehyde, $C_6H_5.CH_2.CHO$, an intermediate product, *distyrolene dioxide*, being first formed, especially when the acid employed is weak; this forms a thick, oily liquid, which boils at 250° under a pressure of 50 mm., and probably has the following constitution:



Chromic acid oxidizes the alcohol to benzaldehyde and benzoic acid; nitric acid, on the other hand, converts it first into benzoylmethyl alcohol, $C_6H_5.CO.CH_2.OH$.[1]

Styrolene chloride, $C_6H_5.C_2H_3Cl_2$, is formed by the direct combination of styrolene with chlorine, but is difficult to purify since substitution products are simultaneously formed. It is a thick, oily liquid, which decomposes on distillation, and is scarcely soluble in water, but imparts to it a very characteristic penetrating smell and taste, resembling those of the oils of lemons and juniper berries (Blyth and Hofmann).

Styrolene bromide, $C_6H_5.C_2H_3Br_2$, was also prepared by Blyth and Hofmann, and has the same characteristic smell and taste as the chloride. It is best obtained by mixing styrolene with an equal volume of chloroform,[2] or with two volumes of ether,[3] and adding the calculated quantity of bromine to the well-cooled liquid. It may also be prepared by adding bromine gradually to hot ethylbenzene,[4] and purifying the product by recrystallization (Zincke). It crystallizes from alcohol in small plates or broad needles, melting at 74°—74°·5.

Styrolene iodide, $C_6H_5.C_2H_3I_2$, was obtained by Berthelot, by agitating styrolene with a solution of iodine in potassium iodide. It forms crystals, which are soluble in ether, and readily decompose into iodine and metastyrolene.[5]

Styrolene acetate, $C_6H_5.C_2H_3(C_2H_3O_2)_2$, is prepared by heating

[1] Zincke, *Ann. Chem. Pharm.* ccxvi. 206.
[2] Glaser, *ibid.* cliv. 154.
[3] Zincke, *ibid.* ccxvi. 288.
[4] Radziszewski, *Ber. Deutsch. Chem. Ges.* vi. 493; Friedel and Balsohn, *Bull. Soc. Chim.* xxxv. 55.
[5] *Ibid.* vi. 295; vii. 277.

the bromide with potassium acetate and glacial acetic acid, or the alcohol with acetic anhydride. It is an oily, odourless liquid, boiling at 274° (Zincke).

Styrolene benzoate, $C_6H_5.C_2H_3.(C_7H_5O_2)_2$, crystallizes from hot alcohol or benzene in small, lustrous needles, which melt at 96° —97°, and sublime without decomposition (Zincke).

Styrolene thiocyanate, $C_6H_5.C_2H_3(SCN)_2$, is prepared by boiling the bromide with an alcoholic solution of potassium thiocyanate. It crystallizes from dilute alcohol in yellowish white needles, which melt at 101°—102°. It volatilizes with steam, to which it imparts a peculiar sharp smell, and causes a violent burning pain when placed on sensitive portions of the skin. It combines with benzene to form a compound, which crystallizes in long needles, loses benzene in the air, and melts at 62°.[1]

SUBSTITUTION PRODUCTS OF STYROLENE.

2289 The hydrogen of both the nucleus and the side-chain in styrolene can be replaced, but many substitution derivatives are not prepared from the hydrocarbon, but by different reactions. The only known derivatives in which the hydrogen of the nucleus has been replaced are nitrostyrolene and the methyl ether of the still unknown hydroxystyrolene. The latter will be described first, while nitrostyrolene will be treated along with the other nitro-substitution products.

Orthovinylanisol, $(CH_3O)C_6H_4.CH{=}CH_2$, is formed by heating orthomethyoxyphenylacrylic acid, $(CH_3O)C_6H_4.CH{=}CH.CO_2H$, or better by combining the latter with iodine, and treating the product with a cold solution of sodium carbonate. It is a liquid, which has a similar odour to the higher-boiling portion of coal-tar naphtha, but fainter and more agreeable. It does not solidify in a freezing mixture, and boils at about 195°—200°, the greater portion being thereby converted into a polymeric modification, which can be obtained by heating for an hour at 150° in the form of a transparent, vitreous mass, which is again converted into the monomolecular variety on more strongly heating.

Paravinylanisol has been prepared by Perkin from paramethoxyphenylacrylic acid; it has an odour resembling that of fennel, solidifies on cooling to a crystalline mass, and boils at

[1] Nagel, *Ann. Chem. Pharm.* ccxvi. 323.

about 204°—205°, a partial polymerization taking place, this being completely effected when it is heated to 150° for several hours.[1]

This compound is the lower homologue of anethol, which forms the chief constituent of oil of anise and other similar oils.

Hesperetol, $(CH_3O)C_6H_3(OH)CH{=}CH_2$, is formed by the dry distillation of the hydrated calcium salt of hesperitic acid, $(CH_3O)C_6H_3(OH)C_2H_2.CO_2H$, and forms a crystalline mass, which melts at 57°, and has an agreeable odour recalling those of both guaiacol and styrolene. It forms a splendid carmine-red solution in sulphuric acid.[2]

α-Phenylchlorethylene or *Phenylvinylchloride*, $C_6H_5.CH{=}CHCl$, was first obtained by Stenhouse in an impure condition by the distillation of cinnamic acid with bleaching-powder solution.[3] Glaser, who named it β-chlorstyrol, prepared it by the action of chlorine on a dilute solution of sodium cinnamate, and by heating phenylchlorolactic acid, $C_6H_5.C_2H_2Cl(OH)CO_2H$, with water to 200°—220°.[4] It is also formed by the action of sodium carbonate solution on phenyldichloropropionic acid, $C_6H_5.CHCl.CHCl.CO_2H$,[5] and when phenylacetaldehyde is treated with phosphorus pentachloride, and the product of this reaction, *α-phenylethidene chloride*, $C_6H_5.CH_2.CHCl_2$, a liquid with a sharp, turpentine-like odour, heated with alcoholic potash.[6]

α-Phenylchlorethylene is a liquid which has a pleasant hyacinth-like odour, and boils at 199°. When it is heated with an alcoholic solution of sodium ethylate, *phenylvinyl ethyl ether*, $C_6H_5.CH{=}CH.OC_2H_5$, is formed as a liquid which boils at 217°, and decomposes on heating with water into ethyl alcohol and phenylacetaldehyde (Erlenmeyer).

β-Phenylchlorethylene, $C_6H_5.CCl{=}CH_2$. When methylphenylketone is treated with phosphorus pentachloride, *β-phenylethidene chloride*, $C_6H_5.CCl_2.CH_3$, is formed, and decomposes on distillation into hydrochloric acid and β-phenylchlorethylene. This is a liquid, which boils at 190°,[7] and is converted into

[1] Perkin, *Journ. Chem. Soc.* 1877, ii. 608 ; 1878, i. 211.
[2] Tiemann and Will, *Ber. Deutsch. Chem. Ges.* xiv. 967.
[3] *Ann. Chem. Pharm.* lv. 3 ; lvii. 79.
[4] *Ibid.* cliv. 164.
[5] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xiv. 1867.
[6] Forer, *ibid.* xvii. 982.
[7] Friedel, *Bull. Soc. Chim.* i. 7.

phenylacetylene, $C_6H_5.C{\equiv}CH$, by heating to 120° with alcoholic potash, while the *a*-compound loses no chlorine even at 200° when subjected to the same treatment, but is only partially converted into a resinous mass (Glaser). A similar relation is shown by the two chloropropylenes.[1]

a-Phenylbromethylene or *Phenylvinyl bromide*, $C_6H_5.CH{=}CHBr$, is formed when phenyldibromopropionic acid, $C_6H_5.CHBr.CHBr.CO_2H$, is boiled with water (Glaser), and is an oily liquid, which has a pleasant odour, resembling that of hyacinths, and solidifies at a low temperature to a dazzling white, crystalline mass, melting at + 7°. It boils at 219°—221°, a small quantity of hydrobromic acid being evolved, and combines with bromine to form *bromostyrolene dibromide*, $C_6H_5.CHBr.CHBr_2$, which crystallizes from petroleum-ether in long needles, melting at 37°—38°.[2]

β-Phenylbromethylene, $C_6H_5.CBr{=}CH_2$, is obtained by the action of boiling alcoholic potash on styrolene bromide. It is a heavy oily liquid, the vapour of which produces a flow of tears, and decomposes on distillation, even under diminished pressure (Glaser). When it is heated to 180° with water, methylphenylketone, $C_6H_5.CO.CH_3$, is formed, while the action of sodium and carbon dioxide yields a mixture of phenylpropiolic and phenylpropionic acids, but, contrary to the statement of Swarts, no cinnamic acid.[3]

2290 *a-Phenylnitro-ethylene*, $C_6H_5.CH{=}CHNO_2$, was first prepared by Simon by the direct action of concentrated nitric acid on styrol and was named by him *nitrostyrol*, its composition being subsequently determined by Blyth and Hofmann. The same compound is formed when equal molecules of nitromethane and benzaldehyde are heated to 160° with a little zinc chloride:[4]

$$C_6H_5.CHO + CH_3NO_2 = C_6H_5.CH{=}CHNO_2 + H_2O.$$

It has also been obtained by the action of concentrated nitric acid on phenylcrotonic acid,[5] $C_6H_5.CH{=}CH.CH_2.CO_2H$.

It crystallizes from alcohol in splendid, yellow, rhombic prisms, which melt at 58°. It has a strong smell and taste of cinnamon, produces burns and blisters on the skin, like oil of mustard, is readily volatile with steam, and in the form of

[1] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xii. 1609.
[2] Fittig and Binder, *Ann. Chem. Pharm.* cxcv. 114.
[3] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xvi. 152.
[4] Priebs, *Ann. Chem. Pharm.* ccxxv. 319.
[5] H. Erdmann, *Ber. Deutsch. Chem. Ges.* xvii. 412.

vapour attacks the eyes and nose most violently. In the compact state it scarcely dissolves in caustic soda, but when finely divided it dissolves completely and is reprecipitated by acids. When sodium nitrite and then dilute sulphuric acid are added to the alkaline solution, the nitrolic acid reaction takes place, being probably caused by liberation of nitromethane. On heating to 100° with concentrated hydrochloric acid, it decomposes with formation of phenylchloracetic acid and hydroxylamine:

$$C_6H_5.CH{=}CHNO_2 + H_2O + HCl = C_6H_5.CHCl.CH_2.CO_2H + N(OH)H_2.$$

Crystals of *a*-phenylnitro-ethylene change in the light to a dull white, polymeric body, which crystallizes from hot alcohol in rhombic plates or needles with a satin lustre. This substance is not identical with the nitrometastyrol, which Blyth and Hofmann prepared by the nitration of metastyrol and described as an amorphous powder, insoluble in alcohol.

Phenylnitro-ethylene chloride, $C_6H_5.CHCl.CHCl(NO_2)$, is prepared by passing chlorine into a cooled solution of phenylnitro-ethylene in chloroform. On the evaporation of the latter, it remains as a thick oil, which has a penetrating odour, resembling when dilute that of pippins. On standing for some time, large lustrous crystals are deposited, which are extremely soluble in ether and chloroform, and are again left on evaporation as an oil, which solidifies, when placed in contact with a fragment of the original crystals, to a mass, which melts at 30°.

Cold caustic soda solution converts it into *phenylchloronitro-ethylene,* $C_6H_5.CCl{=}CHNO_2$, which crystallizes from petroleum spirit in lustrous, golden-yellow plates or tablets, which have a characteristic odour, melt at 48°—49° and, when finely divided, dissolve in alkalis, thus proving that the group $CHNO_2$ is present (Vol. III. Part I. p. 188).

Phenylnitro-ethylene bromide, $C_6H_5.CHBr.CHBr(NO_2)$, is best obtained by bringing the two constituents together in carbon disulphide solution. On evaporation it separates in splendid, monosymmetric crystals, which have a vitreous lustre, melt at 86° and are soluble in alkalis. Caustic soda converts it into *phenylbromonitro-ethylene,* $C_6H_5.CBr{=}CHNO_2$, which crystallizes from petroleum-spirit in golden-yellow, iridescent needles or plates, which melt at 67°—68° and have a characteristic odour, slightly resembling that of hay.

2291 *The Nitrophenylethylenes* or *Nitrostyrolenes*, $C_6H_4(NO_2)CH{=}CH_2$, are formed by the action of hot carbonate of sodium solution on the nitrophenylbromopropionic acids, $C_6H_4(NO_2)CHBr.CH_2.CO_2H$, or by heating the lactones of the nitrophenyllactic acids, which are also obtained from these bodies:

$$C_6H_4(NO_2)CH\begin{matrix}CH_2\\ \diagup\quad\diagdown\\ O\end{matrix}CO = C_6H_4(NO_2)CH{=}CH_2 + CO_2.$$

Orthonitrostyrolene is an oil, which is volatile with steam, has a characteristic odour and solidifies on cooling to a splendid crystalline mass, melting at 12°—13°·5. It is coloured blue when heated with concentrated sulphuric acid and forms a crystalline dibromide, melting at 52°.[1]

Metanitrostyrolene has an agreeable, cinnamon-like smell and melts at −5°; its dibromide forms crystals, which melt at 78°—79°.[2]

Paranitrostyrolene crystallizes from petroleum-spirit in yellowish, strongly refractive prisms, which melt at 29°, smell like oil of cinnamon and have a burning, bitter, but slightly sweet taste. It changes into an insoluble polymeric modification on standing. Its dibromide melts at 72°—73°.[3]

Paranitrophenylnitro-ethylene, $C_6H_4(NO_2)CH{=}CHNO_2$, which is also known as *ω-4-dinitrostyrol*, is easily prepared by the elimination of carbon dioxide from paradinitro-cinnamic acid,[4] $C_6H_4(NO_2)CH{=}C(NO_2)CO_2H$, and is also formed, together with the ortho-compound, by the nitration of phenylnitroethylene (Priebs). It crystallizes from acetone in yellow plates and from alcohol in needles, which melt at 199°, sublime when carefully heated and are volatile with steam.

It is oxidized to paranitrobenzoic acid by chromic acid solution and is decomposed by warming with sulphuric acid, carbon monoxide being evolved and paranitrobenzaldehyde and hydroxylamine sulphate formed:

$$C_6H_4(NO_2)CH{=}CHNO_2 + H_2O = C_6H_4(NO_2)CHO + N(OH)H_2 + CO.$$

These then combine to some extent to form paranitrobenzaldoxime.

[1] Einhorn, *Ber. Deutsch. Chem. Ges.* xvi. 2213.
[2] Prausnitz, *ibid.* xvii. 597.
[3] Basler, *ibid.* xvii. 3005.
[4] Friedländer and Mähly, *ibid.* xvi. 848; *Ann. Chem. Pharm.* ccxxix. 224.

Paranitrophenylnitro-ethylene bromide, $C_6H_4(NO_2)CHBr.CHBr(NO_2)$, forms colourless, lustrous plates, melting at 102°—103°.

Metanitrophenylnitro-ethylene or *ω-3-Dinitrostyrolene*, is a product of the decomposition of the very unstable metadinitrocinnamic acid and crystallizes from alcohol in yellowish plates, which melt at 122°. It behaves towards chromic and sulphuric acids similarly to the para-compound. If it be dissolved in alcohol and treated successively with caustic soda solution and bromine water, *metanitrophenylethoxydibromonitro-ethane*, $C_6H_4(NO_2)CH(OC_2H_5)CBr_2NO_2$, is formed, and is deposited in lustrous plates, melting at 98°—99°.[1]

Orthonitrophenylnitro-ethylene is more readily soluble in alcohol than the para-compound and crystallizes in distorted yellow needles, which melt at 106°—107° and are volatile with steam. Alkaline permanganate oxidizes it to orthonitrobenzoic acid. Its dibromide forms white needles, melting at 90°—90·°5 (Preibs).

Orthonitrophenylchlorethylene or *Orthonitrophenylvinyl chloride*, $C_6H_4(NO_2)CH{=}CHCl$, is formed by the action of hypochlorous acid on sodium orthonitro-cinnamate :

$$C_6H_4(NO_2)CH{=}CH.CO_2Na + ClOH = C_6H_4(NO_2)CH{=}CHCl + CO_3NaH.$$

It crystallizes from hot alcohol in lustrous, yellowish needles, or prisms, melting at 58°—59°, has a pleasant odour and produces a burning pain when placed on the skin.

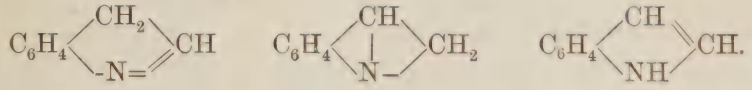
Orthamidophenylvinyl chloride, $C_6H_4(NH_2)CH{=}CHCl$, is obtained by the reduction of the preceding compound with tin and hydrochloric acid. It is slightly soluble in cold, more readily in hot water and alcohol and crystallizes in prisms, which have a peculiar but not unpleasant smell.[2] On heating with sodium ethylate it is converted into indol.

2292 *Indol*, C_8H_7N, was first prepared by Baeyer by heating oxindol, C_8H_7NO (p. 21), with zinc dust.[3] He then found that it can also be obtained directly from indigo by heating with tin, or zinc, and hydrochloric acid, and distilling the yellow reduction product with zinc dust, and he therefore looked upon it as the mother substance of indigo.[4] It was shortly afterwards prepared by Baeyer and Emmerling by heating orthonitrocinnamic acid with caustic potash and iron filings;[5]

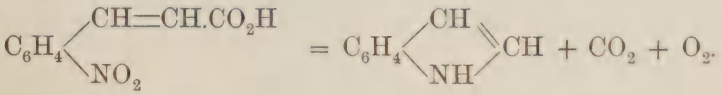
[1] Eriedländer and Lazarus, *Ber. Deutsch. Chem. Ges.* ccxxix. 233.
[2] Lipp, *ibid.* xvii. 1070. [3] *Ann. Chem. Pharm.* cxl. 295.
[4] *Ber. Deutsch. Chem. Ges.* i. 17; *Ann. Chem. Pharm.* Suppl. vii. 56.
[5] *Ber. Deutsch. Chem. Ges.* ii. 679.

and Baeyer and Caro found that it is formed in small quantity when aniline is passed through a red-hot tube.[1] Methylethylaniline and diethylaniline give a somewhat better yield, and a still larger amount is obtained when dimethylorthotoluidine and especially diethylorthotoluidine, are employed, while diethylparatoluidine does not give a trace.[2] It is formed in large quantity, however, when the vapour of cumidine, or orthamidoisopropylbenzene, $C_6H_4(NH_2)CH(CH_3)_2$, is passed over heated lead oxide,[3] and is also obtained when oxalorthotoluidic acid, $CH_3.C_6H_4.NH.CO.CO.OH$, is heated with zinc dust, or when its barium salt is submitted to dry distillation.[4]

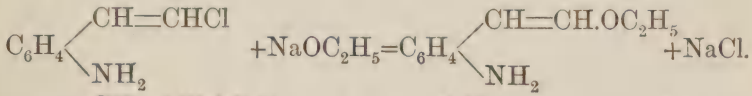
It is derived from oxindol, the anhydride of orthamidophenylacetic acid, by a simple elimination of oxygen; according to this reaction its constitution could be expressed by any one of the following formulæ:

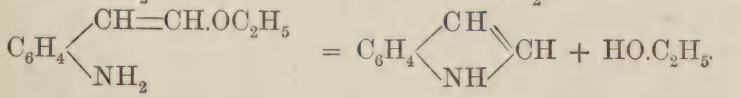


Its formation from orthonitro-cinnamic acid is in favour of the last of these:



The careful study of its reactions has proved that it contains the imido-group and it can therefore be looked upon as the anhydride of the unknown orthamidophenylvinyl alcohol, which, like other similar ortho-amido-compounds does not exist in the free state. Its chloride, however, is known, and has already been described, and Lipp has shown that this is converted into indol when heated with sodium ethylate.[5] Orthamidophenylvinyl ether is probably first formed, but decomposes immediately into ethyl alcohol and indol:





[1] *Ber. Deutsch. Chem. Ges.* x. 692. [2] *Ibid.* x. 1262.
[3] Fileti, *ibid.* xvi. 2928.
[4] Mauthner and Suida, *Monatsh. Chem.* vii. 230.
[5] *Ber. Deutsch. Chem. Ges.* xvii. 1067.

It is also formed by the fusion of albuminoid substances with caustic potash,[1] and by the pancreatic fermentation of the same,[2] so that it occurs, together with its homologue skatol, C_9H_9N, in human excrement; it is only present however in small quantity, since it is for the most part converted into indoxylsulphuric acid, $C_8H_6NSO_4H$, which is excreted with the urine (p. 40).

Indol is readily soluble in alcohol, ether and hydrocarbons, and tolerably in hot water, from which it separates on cooling in oily drops, which subsequently form plates, similar to those of benzoic acid. It crystallizes from petroleum-spirit in large plates, which melt at 52° and have a satin lustre. It is volatile with steam and boils with partial decomposition at 245°—246°, so that the determination of its vapour density always gives high values, 4·33—4·62 instead of 4·05.[3]

It possesses a characteristic, disagreeable and persistent odour. When an aqueous solution of indol is treated with sodium nitrite solution acidified with sulphuric acid, or with a little red fuming nitric acid, a red precipitate consisting of microscopic crystals is formed, which has the composition $C_{16}H_{13}(NO)N_2.NO_3H$ (Nencki),[4] while large red needles of a different compound are deposited when nitrogen trioxide is passed into an alcoholic solution. A pine splinter moistened with hydrochloric acid is coloured deep cherry-red by a solution or the vapour of indol (Baeyer).

Indol suspended in water is partly oxidized to indigo blue, $C_{16}H_{10}N_2O_2$, by the action of air containing ozone, while the remainder is converted into a resinous mass (Nencki).

Indol is a weak base and forms a salt with hydrochloric acid, which is only slightly soluble and is decomposed by boiling with water.

Indol picrate, $C_8H_7N.C_6H_3(NO_2)_3O$. This characteristic compound is formed when its constituents are brought together in benzene solution. It crystallizes in long, red needles, which are scarcely soluble in petroleum-spirit, slightly in cold but readily in hot benzene and are decomposed by ammonia.[5]

2293 *Methylindol*, $C_8H_6N.CH_3$. Pyroracemic acid combines with methylphenylhydrazine to form methylphenylhydrazine-

[1] Engler and Janecke, *Ber. Deutsch. Chem. Ges.* ix. 1411; Nencki, *Journ. Prakt. Chem.* [2], xvii. 98.

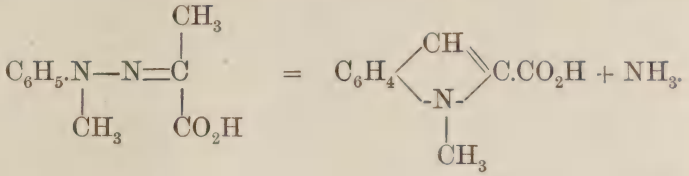
[2] Nencki, *Ber. Deutsch. Chem. Ges.* vii. 1593; viii. 336; Brieger, Hoppe-Seyler's *Zeitschr.* iii. 141.

[3] Nencki, *Ber. Deutsch. Chem. Ges.* viii. 1517.

[4] *Ibid.* viii. 722.

[5] Baeyer and Caro, *ibid.* x. 1263; Baeyer, *ibid.* xii. 1314.

pyroracemic acid, which is quantitatively decomposed by hydrochloric acid into ammonia and methylindolcarboxylic acid:



This substance decomposes on continued heating into carbon-dioxide and methylindol; the latter is an oily liquid, which boils at 239°, does not solidify at —20° and smells like the aromatic bases and not like indol. It dissolves in concentrated hydrochloric acid and is reprecipitated by water; it behaves towards fuming nitric acid and nitrous acid in the same way as indol, and colours a pine splinter moistened with hydrochloric acid a deep reddish violet.

Methylindol picrate, $C_8H_6N(CH_3)C_6H_3(NO_2)_3O$, is readily soluble in hot benzene, less readily in ether and crystallizes from the latter in splendid dark-red prisms, which melt at 150° and are decomposed by water, especially on warming.

Ethylindol, $C_8H_6N.C_2H_5$, has been prepared from ethylphenylhydrazine; it boils at about 247° and can scarcely be distinguished by its other properties from methylindol.

Phenylindol, $C_8H_6N.C_6H_5$, is a heavy oil, which has been obtained from diphenylhydrazine; it colours an acidified pine splinter a deep bluish violet.[1]

The following indols have been prepared from the methyl- and ethyl-derivatives of the tolylhydrazines:[2]

	Boiling-point.
Methylorthotolindol, $C_8H_5(CH_3)N.CH_3$ . . .	—
Methylparatolindol, $C_8H_5(CH_3)NCH_3$	242°—245°
Ethylparatolindol, $C_8H_5(CH_3)NC_2H_5$	253°—255°

Benzylindol, $C_8H_6N.CH_2.C_6H_5$, was obtained from benzylaniline, by converting this into the hydrazine and treating it as described above. It crystallizes from alcohol in compact needles, which melt at 44°·5 and only have a faint smell. It gives a reddish violet colouration with the pine-wood test.

Acetylindol, $C_8H_6NCO.CH_3$, is formed by heating indol with

[1] Fischer and Hess, *Ber. Deutsch. Chem. Ges.* xvii. 589.
[2] Hegel, *Ann. Chem. Pharm.* ccxxxii. 214.
[3] Antrick, *ibid.* ccxxvii. 360.

acetic anhydride; it is readily soluble in benzene and crystallizes from hot water in long needles, which melt at 182°—183° and sublime in four-sided, truncated pyramids.[1]

2294 *Indoxyl*, C_8H_7NO, was first observed as a product of the decomposition of indoxylsulphuric acid.[2] Baeyer then obtained it from *indoxylic acid*, $C_8H_6NO(CO_2H)$, which is formed by the reduction of orthonitrophenylpropiolic acid, $C_6H_4(NO_2)C{\equiv}C.CO_2H$, and decomposes into carbon dioxide and indoxyl on boiling with water.[3] It is a brown oil, which is not volatile with steam, is readily converted into a resinous mass and dissolves slightly in hot water, forming a solution which shows a yellowish green fluorescence. It is simultaneously an acid and a base; its alkaline solution absorbs oxygen from the air with formation of indigo-blue, which is also formed when ferric chloride is added to its solution in hydrochloric acid.

Nitroso-indoxyl, $C_8H_6(NO)NO$, is obtained in fine, yellowish needles, when indoxyl is treated with sodium nitrite and then dilute hydrochloric acid.[4]

Ethylindoxyl, $C_8H_6NO(C_2H_5)$, is formed when ethylindoxylic acid, $C_8H_5.NO(C_2H_5)CO_2H$, is heated and is a colourless liquid, which is volatile with steam, smells like indol and colours pine-wood moistened with hydrochloric acid a brownish red. It also forms a nitrosamine, crystallizing in yellowish needles, and is converted into indigo-blue by oxidation.

Phenylazo-indoxyl, $C_{14}H_{14}N_3O$, is obtained by adding a solution of diazobenzene chloride to an aqueous solution of indoxyl. It crystallizes from alcohol in thick, orange-coloured prisms, which have a fine yellowish green, metallic lustre and melt at 236° with decomposition; it forms a reddish brown solution in caustic soda, from which it is reprecipitated by carbon dioxide.

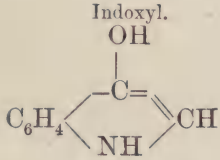
Indoxylsulphuric acid, $C_8H_6N.O.SO_2.OH$. After Schunck had proved that indigo is not contained as such in the plants from which it is obtained, but is formed by the decomposition of a glucoside, which he named indican, he also endeavoured to isolate the substance which yields the indigo which is sometimes found in urine. He was unable to obtain it in the pure state, but thought it probable that it was also a glucoside and perhaps identical with indican.[5] According to Hoppe-Seyler, it is an invariable constituent of the urine of Herbivora, and always

[1] Baeyer, *Ber. Deutsch. Chem. Ges.* xii. 1314.
[2] Baumann and Tiemann, *ibid.* xii. 1098.
[3] Baeyer, *ibid.* xiv. 1741. [4] *Ibid.* xvi. 2188.
[5] *Mem. Manchester Lit. Phil. Soc.* xiv. 239; *Jahresber. Chem.* 1857, 564.

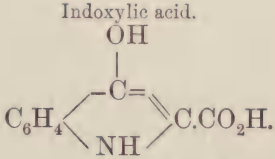
occurs, although in very small quantity, in normal human urine, but in larger quantities during certain diseases.[1] It increases during a diet of albumen, and since this food yields indol when subjected to the pancreatic fermentation, the latter appeared to be the source of the "urine-indican," a supposition which was confirmed by the fact that the amount of urine-indican increased largely when indol was administered.[2] Baumann then showed that the substance found in the urine is quite different from vegetable indican.[3] He and Brieger succeeded in obtaining it in larger quantity from the urine of a dog, to which 15 grammes of indol were administered in the course of five days.[4] They found that it is the potassium salt of indoxylsulphuric acid, and investigated it more thoroughly.[5] Baeyer then prepared it by heating a solution of indoxyl with potassium disulphate.[6] It is readily soluble in water, slightly in cold alcohol and crystallizes from hot alcohol in lustrous plates or tablets, which decompose on heating with dilute acids into indoxyl and acid potassium sulphate, but are not attacked by caustic potash solution even at 170°. When the dry salt is heated, indigo-blue sublimes, and this is quantitatively formed when the solution is warmed with ferric chloride and hydrochloric acid (Baumann and Tiemann).

Indoxyl contains the imido-group, since it forms a nitrosamine, and also a hydroxyl-group, as is proved by the formation of indoxylsulphuric acid. The constitutions of the compounds mentioned above are expressed by the following formulæ:

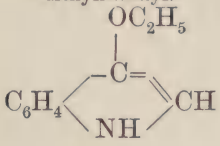
Indoxyl.



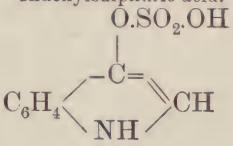
Indoxylic acid.



Ethylindoxyl.

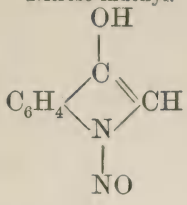


Indoxylsulphuric acid.

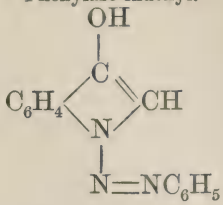


[1] *Arch. Pathol. Anatomie*, xxvii. 388.
[2] Jaffé, *Centralblatt med. Wissenschaft*, 1872, 2.
[3] *Pflüger's Arch.* xiii. 291.
[4] *Hoppe-Seyler's Zeitschr.* iii. 254.
[5] *Ber. Deutsch. Chem. Ges.* xii. 1098.
[6] *Ibid.* xiv. 1745.

Nitroso-indoxyl.



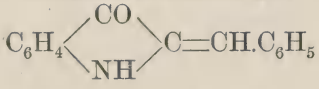
Phenylazo-indoxyl.



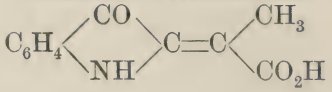
Indoxyl can therefore be looked upon as the anhydride of orthamidostyrolene alcohol.

2295 *The Indogenides.* Baeyer has given this name to the compounds which are formed by the action of aldehydes or ketonic acids upon indoxyl or indoxylcarboxylic acid, as, for example:

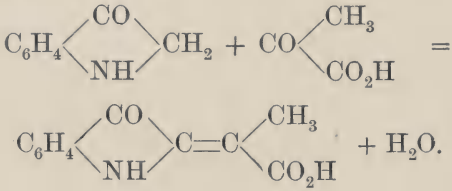
Indogenide of Benzaldehyde.



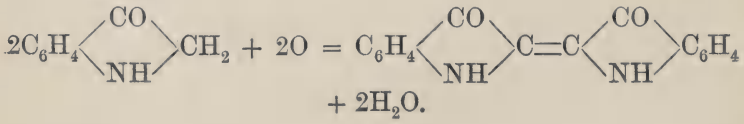
Indogenide of Pyroracemic acid.



In order to explain their formation, Baeyer assumes that the indoxyl passes first into pseudo-indoxyl, which is incapable of existence in the free state, and that this reacts in the case of pyroracemic acid, for example, in the following way:



Pseudo-isatoxime, which was formerly known as nitroso-indoxyl, is formed in a similar manner by the action of nitrous acid. These compounds will be subsequently described. They contain the divalent radical *indogen*, and indigo-blue itself is *di-indogen*, which is formed from indoxyl by the oxidation of the pseudo-indoxyl which is first formed:



PHENYLGLYCOLYL-COMPOUNDS.

2296 *Phenylhydroxyacetic acid*, $C_6H_5.CH(OH)CO_2H$, was first prepared by Winckler by heating extract of bitter almonds with hydrochloric acid, and was called mandelic acid.[1] This reaction is the first instance of the synthesis of a hydroxy-acid from hydrocyanic acid and an aldehyde. Liebig, who considered the discovery of this acid as one of the most important additions which had recently been made to organic chemistry, writes upon its formation:

"Mandelic acid is formed when hydrochloric acid is evaporated with a mixture of hydrocyanic acid and benzoyl hydride; in addition to this product ammonia is formed and remains combined with the hydrochloric acid.

"The nitrogen of the hydrocyanic acid must be contained in the ammonia and its other constituents in the mandelic acid. It is already well known, that when hydrocyanic acid is decomposed by the action of mineral acids or strong bases, formic acid is formed on the one hand, and ammonia set free on the other.

"If the constituents of formic acid be actually subtracted from the formula of mandelic acid, that of benzoyl hydride remains.

"This acid is therefore built up by the combination of the formic acid at the moment of its formation with benzoyl hydride." [2]

Laurent obtained the same acid by the action of fuming sulphuric acid on crude oil of bitter almonds and named it *acide formobenzoïlique*.[3] Wöhler found that it is also formed when amygdalin is heated with fuming nitric acid,[4] but Lewkowitsch has shown that the acid prepared by this method is optically active and stands in the same relation to that obtained from oil of bitter almonds as lævotartaric acid to ordinary tartaric acid.[5]

Several methods have been proposed for its preparation from benzaldehyde and hydrocyanic acid.[6] According to Spiegel it

[1] *Ann. Chem. Pharm.* xviii. 310.
[2] *Ibid.* xviii. 319.
[3] *Ann. Chim. Phys.* [2], lxv. 202.
[4] *Ann. Chem. Pharm.* lxvi. 238.
[5] *Ber. Deutsch. Chem. Ges.* xvi. 1565, 1568 and 2721.
[6] Naquet and Luginin, *Ann. Chem. Pharm.* cxxxix. 299; Wallach, *ibid.* cxciii. 38.

is most simply obtained by moistening rather more than one molecule of pure potassium cyanide with a little water, pouring one molecule of benzaldehyde upon it and then allowing one molecule of hydrochloric acid, in the form of the fuming aqueous acid, to drop slowly into the well-agitated and cooled mixture. The phenylhydroxyacetonitril, $C_6H_5.CH(OH)CN$, thus formed is heated for two hours to 130°—140° with two volumes of hydrochloric acid saturated at 0°, and the phenylchloracetic acid, $C_6H_5.CHCl.CO_2H$, which is the product of this reaction, finally converted into mandelic acid by boiling with a caustic alkali or an alkaline carbonate.[1]

It crystallizes in rhombic needles or large tablets, which melt at 118° and are readily soluble in alcohol, ether and water; 100 parts of the last dissolve 15·97 parts at 20° (Lewkowitsch). It has a faint odour resembling that of sweet almonds and tastes strongly acid and then somewhat styptic. It is oxidized to benzoic acid by nitric acid, while carbon dioxide and benzaldehyde are formed when its aqueous solution is boiled with manganese dioxide.. Benzaldehyde is also a product of its decomposition by dry distillation (Liebig) and is formed, accompanied by formic acid, when it is heated to 130° with dilute sulphuric acid.[2]

When a solution of mandelic acid is neutralized with cinchonin and concentrated, the salt of the dextro-rotatory acid is the first to separate out.

Lævomandelic acid is also formed, as already mentioned, when amygdalin is heated for several hours on the water-bath with fuming hydrochloric acid, black humus-like substances being also formed. The acid is extracted from the filtrate with ether. It forms rhombic crystals, which do not melt until 132°·8 and are less soluble in water than the inactive acid, 100 parts only dissolving 8·64 parts at 20°.

The growth of *Penicillium glaucum* in a nutritive solution containing the inactive acid causes its decomposition in such a way that the lævo-rotatory acid is used for the building up of the cells, while the dextro-acid remains behind. Another fungus exerts exactly the opposite action and only assimilates the dextro-acid.

Dextromandelic acid has the same melting-point, the same solubility and the same rotating power, but of the opposite sign,

[1] Naquet and Luginin, *Ann. Chem. Pharm.* cxl. 239.
[2] Biedermann, *Ber. Deutsch. Chem. Ges.* xix. 638.

as the lævo-acid. When equal parts of the two modifications are dissolved in water and the solution concentrated, the ordinary inactive variety, melting at 118°, crystallizes out. They also pass into the latter when heated for thirty hours to 160°, a portion being decomposed with formation of benzaldehyde (Lewkowitsch).

2297 *Potassium phenylhydroxyacetate*, $C_8H_7O_3K$, is very readily soluble in water and alcohol, and remains on evaporation as a soft, friable mass somewhat resembling soap, which has hardly the taste of a salt but tastes and smells faintly like sweet almonds.

Barium phenylhydroxyacetate, $(C_8H_7O_3)_2Ba$, is less soluble in water than the potassium salt and readily crystallizes in very short, thin prisms.

Lead phenylhydroxyacetate, $(C_8H_7O_3)_2Pb$, is a crystalline precipitate, scarcely soluble in water.

Copper phenylhydroxyacetate, $(C_8H_7O_3)_2Cu$, forms a fine, light-blue, almost insoluble powder.

Silver phenylhydroxyacetate, $C_8H_7O_3Ag$, is a white, crystalline precipitate, which is soluble in boiling water, from which it separates in yellowish crystals, resembling those of benzoic acid.

Methyl phenylhydroxyacetate, $C_8H_7O_3(CH_3)$, is very readily soluble in alcohol and crystallizes from a mixture of benzene and petroleum spirit in small, lustrous plates, which melt at 47°—49°.[1]

Ethyl phenylhydroxyacetate, $C_6H_5.CH(OH)CO_2.C_2H_5$. When hydrochloric acid is passed into a solution of phenylhydroxyacetonitril in absolute alcohol, the phenylhydroxyacetimido-ether separates out in needles; this substance is decomposed by water in the following manner:

$$C_6H_5.CH(OH)\begin{cases} NH_2Cl \\ OC_2H_5 \end{cases} + H_2O = C_6H_5.CH(OH)CO.OC_2H_5 + NH_4Cl$$

Ethyl phenylhydroxyacetate is a heavy, strongly refractive liquid, which smells strongly of jasmine, and boils at 253°—255°. It solidifies in a freezing mixture to a crystalline mass, which becomes liquid again at the ordinary temperature.[2]

[1] Baeyer and Zincke, *Ber. Deutsch. Chem. Ges.* xiii. 636.
[2] Beyer, *Journ. Prakt. Chem.* [2], xxxi. 382.

Phenylchloracetic acid, $C_6H_5.CHCl.CO_2H$, was prepared by Radziszewski from mandelic acid by the action of hydrochloric acid at 140°.[1] It may be more easily obtained as described above, by the action of hydrochloric acid on phenylhydroxy-acetonitril. It crystallizes in rhombic plates, melting at 78°. It is readily converted into mandelic acid by alkalis and is reduced to phenylacetic acid by the action of sodium amalgam on its alcoholic solution, or more simply when its ammoniacal solution is treated with zinc dust, the reaction being accompanied by a considerable evolution of heat (Spiegel).

Methyl phenylchloracetate, $C_6H_5.CHCl.CO_2.CH_3$, is obtained by the action of hydrochloric acid on a solution of the acid in methyl alcohol, as an oily liquid, which attacks the eyes violently and boils with slight decomposition at 248°.[2]

Phenylbromacetic acid, $C_6H_5.CHBr.CO_2H$, is formed when mandelic acid is heated with fuming hydrobromic acid to 120°—130°,[3] as well as by the action of bromine at 150° on phenylacetic acid (Radziszewski). It separates from carbon disulphide in large, monosymmetric crystals, melting at 83°—84°.

Methylmandelic acid, $C_6H_5.CH(OCH_3)CO_2H$, has been prepared by the action of sodium methylate on the methyl ether of phenylchloracetic acid. It crystallizes from petroleum-ether in small tablets, melting at 71°—72°, and forms salts which crystallize well (Meyer and Boner).

Phenylmandelic acid, $C_6H_5.CH(OC_6H_5)CO_2H$, is obtained by the action of sodium phenate on methyl phenylchloracetate. It crystallizes from hot water in fascicular groups of fine needles, melting at 108° (Meyer and Boner).

Mandelic acid chloralide, $C_{10}H_7Cl_3O_3$. Mandelic acid, like other hydroxy-acids, combines with chloral on heating to form a chloralide (Vol. III. Part. II. 147):

$$C_6H_5.CH\begin{matrix}OH\\CO_2H\end{matrix} + COH.CCl_3 = C_6H_5.CH\begin{matrix}-O-\\CO_2\end{matrix}CH.CCl_3 + H_2O.$$

This compound separates from chloroform in large crystals, melts at 82°—83° and boils with slight decomposition at 305°—310°.[4]

[1] *Ber. Deutsch. Chem. Ges.* ii. 208.
[2] Meyer and Boner, *ibid.* xiv. 2391.
[3] Glaser and Radziszewski, *Zeitschr. Chem.* 1868, 142.
[4] Wallach, *Ann. Chem. Pharm.* cxciii. 40.

2298 *Phenylamido-acetic acid* or *Phenylglycocoll*, $C_6H_5.CH(NH_2)CO_2H$, is obtained by heating phenylbromacetic acid with ammonia to 100°—110°,[1] and by boiling its nitril with dilute sulphuric acid. The latter is formed by the action of alcoholic ammonia on phenylhydroxyacetonitril and is a crystalline, unstable substance.[2]

Phenylamido-acetic acid is only slightly soluble in the ordinary solvents; it is precipitated from an ammoniacal solution by hydrochloric acid in nacreous plates, which melt at 256°, when heated in a capillary tube; when a test tube is employed the acid sublimes without fusing, while on rapid distillation it decomposes into carbon dioxide and benzylamine (Vol. III. Part IV. 113).

It can also be readily obtained from hydrobenzamide (Vol. III. Part IV. 139), which combines at a low temperature with anhydrous hydrocyanic acid:

$$\left.\begin{matrix} C_6H_5.CH{=}N \\ C_6H_5.CH{=}N \end{matrix}\right\rangle CHC_6H_5 + 2HCN = \left.\begin{matrix} C_6H_5.CH.NH \\ C_6H_5.CH.NH \end{matrix}\right\rangle \begin{matrix} CN \\ CH.C_6H_5. \\ CN \end{matrix}$$

The crystalline substance thus formed melts at 55°. When it is slightly heated with fuming hydrochloric acid for some days, until a clear solution is produced on the addition of water, and then boiled for some hours, phenylamido-acetic acid is formed.[3]

Nitrous acid converts the amido-acid into mandelic acid, which is also formed from it by the pancreatic fermentation. Phenylamido-acetic acid, like other amido-acids, combines with both acids and bases.

Phenylmethylamido-acetic acid or *Phenylsarcosin*, $C_6H_5.CH(NH.CH_3)CO_2H$. When phenylhydroxyacetonitril is allowed to stand for some hours at 60°—80° with an alcoholic solution of methylamine, the nitril, $C_6H_5.(CHNH.CH_3)CN$, is formed and yields phenylsarcosin hydrochloride on heating with hydrochloric acid. The free phenylsarcosin is liberated from this by ammonia; it crystallizes from hot water in fine plates, which sublime when heated, without fusing.[4]

Phenylhydroxyacetamide, $C_6H_5.CH(OH)CO.NH_2$. The forma-

[1] Stöckenius, *Ber. Deutsch. Chem. Ges.* xi. 2002.
[2] Tiemann, *ibid.* xiii. 387.
[3] Plöchl, *ibid.* xiii. 2118.
[4] Tiemann and Piest, *ibid.* xiv. 1982.

tion of a crystalline substance by the action of moist chlorine on oil of bitter almonds was first observed by Stange, and it was mistaken for benzoïn (Vol. III. Part IV. 129) by Robiquet and Boutron-Charlard, who obtained it by the same method from crude oil of bitter almonds, peach kernels and cherry laurel leaves. Winkler, however, found that it differs from this, and was confirmed by Liebig, who analysed the substance and named it "*benzoylhydride benzoate*," $C_{21}H_{18}O_4$. Laurent then prepared it by the action of fuming sulphuric acid on oil of bitter almonds, and determined its formula as $C_{28}H_{24}O_6$; in conjunction with Gerhardt, he subsequently corrected this to $C_{22}H_{18}O_4$ and named the body "*stilbous acid*" (*acide stilbeux*). Gmelin[1] afterwards suggested the formula, $C_{15}H_{12}O_3$.

Zinin was the first to discover that the substance in question contains nitrogen and has the formula, $C_{15}H_{13}NO_2$, and he also found that it is always formed when oil of bitter almonds, which still contains hydrocyanic acid, is brought into contact with a strong acid. Hydrochloric acid, which was the active agent in the production of the body by the action of chlorine, is the most convenient acid to employ. A further quantity can be obtained by the addition of hydrocyanic acid to the clear liquid from which the product has separated. It is scarcely soluble in water, only slightly in alcohol, and forms a crystalline powder, or when slowly deposited from solution in alcohol or acetic acid, four-sided prisms, melting at 195°. On heating with water to 180°, it decomposes into benzaldehyde and the amide of mandelic acid.[2] It is, therefore, *benzidenephenylhydroxyacetamide*, and is formed by the combination of benzaldehyde with the nitril of mandelic acid. The decomposition by water proceeds according to the following equation:

$$C_6H_5.CH(OH)CO.N{=}CH.C_6H_5 + H_2O = C_6H_5.CH(OH)CO.NH_2 + CHO.C_6H_5.$$

Phenylhydroxyacetamide is also formed by the action of ammonia on the ethyl ether of mandelic acid and by heating phenylhydroxyacetimido-ether hydrochloride (Beyer).

$$C_6H_5.CH(OH)C\begin{matrix}=NH_2Cl\\ \diagdown OC_2H_5\end{matrix} = C_6H_5.CH(OH)CO.NH_2 + C_2H_5Cl.$$

[1] *Handbuch Organ. Chem.* iii. 138, where the literature of the subject is referred to.

[2] *Jahresber. Chem.* 1868, 624.

It crystallizes from hot water in rhombic tablets, melting at 132°.

Phenylhydroxyacetonitril, $C_6H_5.CH(OH)CN$, is, as already mentioned, a constituent of crude oil of bitter almonds. Völkel obtained it from this by evaporating the oil with hydrochloric acid at a temperature below 100°,[1] and O. Müller prepared it by boiling with alcohol the sodium sulphite compound of benzaldehyde together with potassium cyanide.[2] It is also readily formed when benzaldehyde is heated with 20 per cent. hydrocyanic acid,[3] or still more simply by acting upon it with the nascent acid.

It is an oily liquid, which is insoluble in water, but readily soluble in alcohol and ether, solidifies at $-10°$ and decomposes at 170° into hydrocyanic acid and benzaldehyde. It yields styrolylamine on reduction (p. 7).

Phenylhydroxyethenylamidoxime, $C_6H_5.CH(OH)C(NOH)NH_2$, is formed by the combination of the nitril with hydroxylamine, and forms crystals which melt at 158°—159°.[4]

Amygdalin or Glucophenylhydroxyacetonitril, $C_{20}H_{27}NO_{11} + 3H_2O$.

2299 The history of this compound, the first known glucoside, has already been given under benzaldehyde. It occurs in the seeds of the Amygdalaceae, Drupaceae, and Pomaceae; bitter almonds contain 2·8—4 per cent., peach kernels 2·35 per cent., cherry kernels 0·82 per cent., plum kernels 0·96 per cent., and apple pips 0·6 per cent. It also occurs in other parts of these plants, and has been found in the leaves of the cherry laurel (*Cerasus Laurocerasus*), in the bark, flowers, and leaves of the bird-cherry (*Prunus Padus*), in the young shoots of apple and plum trees, in the buds and bark of the mountain ash (*Sorbus Aucuparia*), of the hawthorn, &c. All these portions of the plants yields oil of bitter almonds containing hydrocyanic acid on distillation with water. It has not yet been decided whether the hydrocyanic acid which has been obtained from other plants is also derived from amygdalin. The shrubby members of the Spirea family (*Spiræa aruncus*, *Spiræa sorbifolia*, and *Spiræa japonica*) yield a distillate which contains

[1] *Ann. Chem. Pharm.* lii. 361.
[2] *Ber. Deutsch. Chem. Ges.* iv. 980.
[3] Tiemann and Friedländer, *ibid.* xiv. 1967.
[4] Gross, *ibid.* xviii. 1074 and 2477.

hydrocyanic acid, while salicylaldehyde is found in that given by some of the herbaceous plants of the same group.[1] Henry and Boutron-Charland found 0·04 per cent. of hydrocyanic acid in the sap of the bitter cassava (*Manihot utilissima*), which is the source from which arrow-root is prepared, and which is known to be poisonous.[2] It has also been detected in *Chardinia xeranthemoides*, one of the Compositae which occurs in Asia Minor and Persia, in the fruit of *Ximenia americana*, which is an article of food in the tropics, and in *Ipomoea dissecta*, which is indigenous in Trinidad,[3] as well as in *Agaricus oreades*,[4] while the seeds of the vetch (*Vicia sativa*), which contain no amygdalin, yield both benzaldehyde and hydrocyanic acid,[5] benzaldehyde being also found in the germinating seeds of cress (*Lepidium sativum*).[6]

In order to prepare amygdalin, bitter almonds are freed as far as possible from fatty oil by pressing, and the mass repeatedly extracted with boiling alcohol; the alcohol is then distilled off, and the residue recrystallized from boiling alcohol.

It crystallizes in lustrous plates or scales, or from water in transparent, rhombic prisms, which become anhydrous at 120°, and then melt at 200°, soldifying to an amorphous mass on cooling. At 8°-12° it dissolves in twelve parts of water, while it is soluble in every proportion in boiling water. It is slightly soluble in cold, more readily in boiling alcohol and insoluble in ether. Its solution is lævorotatory. On the addition of emulsin to its aqueous solution, it decomposes into grape sugar and phenylhydroxyacetonitril, which is partially decomposed by distillation into benzaldehyde and hydrocyanic acid. The same decomposition takes place on boiling with dilute hydrochloric acid.

When it is treated with zinc and hydrochloric acid, styrolylamine is formed,[7] while cyanogen chloride and benzidene chloride are obtained by the action of phosphorus pentachloride.[8]

It has a sweet taste, followed by a bitter after-taste. According to Frerichs and Wöhler it is not poisonous; symptoms of

[1] Wicke, *Ann. Chem. Pharm.* lxxxiii. 175.
[2] *Ibid.* xviii. 172.
[3] Flückiger and Hanbury, *Pharmacographia*, II. ed. 250.
[4] v. Lösecke, *Jahresber. Chem.* 1871, 812.
[5] Ritthausen and Kreusler, *Journ. Prakt. Chem.* [2] ii. 333.
[6] Schulze, *ibid.* lxxxvii. 129.
[7] Fileti, *Ber. Deutsch. Chem. Ges.* xii. 297.
[8] Schiff, *Ann. Chem. Pharm.* cliv. 337.

poisoning were only observed in two cases, in which doses of two and five grams. respectively had been administered to dogs, and they then resembled those of prussic acid poisoning, with the difference that they prevailed for six to eight hours without alteration, after which the stupor gradually passed away and the animals soon recovered. The breath of both these animals smelt of hydrocyanic acid, and the same smell was noticeable in the urine after the addition of almond emulsin.[1] According to Moriggia and Ossi, amygdalin exerts a poisonous action even in the absence of emulsin, especially in the case of the graminivora.[2]

Heptacetylamygdalin, $C_{20}H_{20}(C_2H_3O)_7NO_{11}$, was prepared by Schiff by boiling amygdalin with acetic anhydride. It crystallizes from alcohol in long, silky needles, which are insoluble in water.

Amygdalic acid or *Glucomandelic acid*, $C_{20}H_{28}O_{13}$, was obtained by Liebig and Wöhler from amygdalin by boiling it with baryta water:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_{20}H_{28}O_{13} + NH_3.$$

It is a white, crystalline, very deliquescent mass (Schiff), which forms amorphous salts.

The following formulæ explain the constitution of amygdalin and amygdalic acid (Schiff), which are the derivatives of a diglucose:

Amygdalin.

$$O<\begin{matrix}C_6H_7O(OH)_4\\C_6H_7O(OH)_3OCH<\begin{matrix}CN\\C_6H_5\end{matrix}\end{matrix}$$

Amygdalic acid.

$$O<\begin{matrix}C_6H_7O(OH)_4\\C_6H_7O(OH)_3OCH<\begin{matrix}CO_2H\\C_6H_5\end{matrix}\end{matrix}$$

AROMATIC SUBSTITUTION PRODUCTS OF MANDELIC ACID.

2300 *Metanitromandelic acid*, $C_6H_4(NO_2)CH(OH)CO_2H$. The nitril of this acid is formed by the action of nascent hydrocyanic acid on metanitrobenzaldehyde. It is a viscid liquid, which is converted by the action of hydrochloric acid on its solution in a mixture of ether and alcohol into the hydrochloride of nitrophenylimido-ether, $C_6H_4(NO_2)CH(OH)C(NH)O$

[1] Frerichs and Wöhler, *ibid.* xv. 337.
[2] *Ber. Deutsch. Chem. Ges.* ix. 198.

$C_2H_5.HCl$, which crystallizes in needles and is decomposed by water with formation of the ether of nitromandelic acid. This is readily soluble in dilute caustic soda; when this solution is acidified with hydrochloric acid and extracted with ether, the ethereal solution contains free nitromandelic acid, which remains on the evaporation of the ether. It has a strongly acid and intensely bitter taste, is slightly soluble in water, alcohol and ether, and separates from the last on addition of petroleum-spirit in small, yellowish, vitreous rhombohedra, melting at 119°=120°.

Ethyl metanitrophenylhydroxyacetate, $C_6H_4(NO_2)CH(OH)CO_2.C_2H_5$, crystallizes from hot petroleum-spirit in silky needles, melting at 63°.[1]

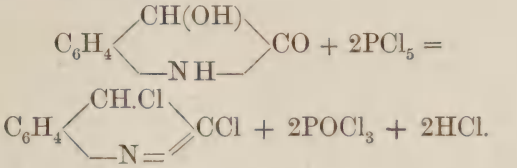
Metanitrophenylamido-acetic acid, $C_6H_4(NO_2)CH(NH_2)CO_2H$, is formed by the action of nitric acid on a solution of amido-mandelic acid in concentrated sulphuric acid. It is readily soluble in hot water and is precipitated by alcohol in fine, pointed, silky needles, which melt with decomposition at 172°. It is converted into metanitromandelic acid by the diazo-reaction.

Metamidophenylamido-acetic acid, $C_6H_4(NH_2)CH(NH_2)CO_2H$, is obtained by the action of tin and hydrochloric acid on the preceding compound. It is precipitated by alcohol from its hot aqueous solution in the form of flat, microscopic needles, which melt with decomposition at 214°. Like the preceding compounds it forms salts with both acids and bases.[2]

Dioxindol, $C_8H_7NO_2$, is the anhydride of orthamidomandelic acid, which is not known in the free state. It was obtained by Knop by the reduction of isatin, which he called *hydridinic acid,*[3] and was then investigated by him and Baeyer.[4] In order to prepare it, a solution of isatin is treated with a little hydrochloric acid and boiled up with zinc dust, the dioxindol being extracted with ether.[5] It dissolves in twelve parts of cold, and six parts of boiling water from which it crystallizes in groups of needles or in transparent, yellow, rhombic prisms, while it is soluble in fifteen parts of cold, and ten of hot absolute alcohol, and crystallizes from this solvent in dazzling white, transparent crystals. It melts at 180° to a violet liquid and decomposes when more strongly heated with formation of

[1] Beyer, *Journ. Prakt. Chem.* [2] xxxi. 382.
[2] Plöchl and Loë, *Ber. Deutsch. Chem. Ges.* xviii. 1179.
[3] *Journ. Prakt. Chem.* xcvii. 65.
[4] *Ann. Chem. Pharm.* cxl. 1.
[5] Baeyer, *Ber. Deutsch. Chem. Ges.* xii. 1309.

aniline. Ammonia colours its alcoholic solution violet, and produces a precipitate of the same colour on boiling, which is soluble in hydrochloric acid. The aqueous solution of dioxindol absorbs oxygen from the air with formation of isatin and isatyde, $C_{16}H_{12}N_2O_4$. Phosphorus pentachloride converts it into chloroxindol chloride (p. 23) :[1]



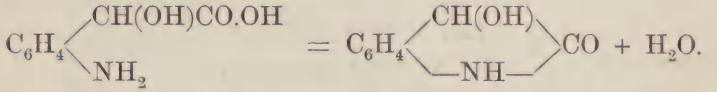
Dioxindol hydrochloride, $C_8H_7NO_2.HCl$, forms warty crusts, readily soluble in water.

Dioxindol sulphate, $C_8H_7NO_2.H_2SO_4 + H_2O$, is obtained by dissolving dioxindol in sulphuric acid ; water precipitates it in white flakes, which dry to a radiating crystalline mass.

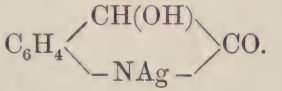
Sodium dioxindol, $C_8H_6NO_2Na + 2H_2O$, is formed by the action of sodium amalgam and water on isatin ; it separates in small cubes, which are slightly soluble in water, less readily in caustic soda solution and are precipitated by a mixture of alcohol and ether in silver-lustrous scales.

Barium dioxindol, $(C_8H_6NO_2)\,Ba + 4H_2O$, is formed by the addition of barium chloride to the solution of sodium dioxindol, as a crystalline precipitate, which separates from a dilute solution in small cubes.

These compounds are probably salts of orthamidomandelic acid, which immediately decomposes into water and dioxindol when liberated by acids :



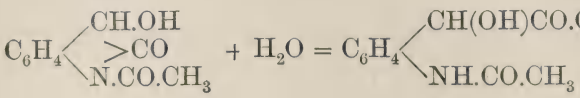
Silver dioxindol, $C_8H_6NO_2Ag$, is obtained as a white crystalline precipitate, when ammonia is added to a solution of sodium oxindol and silver nitrate. It is an unstable substance, which decomposes in the moist state with formation of benzaldehyde and metallic silver, and probably has the following constitution :



[1] *Ber. Deutsch. Chem. Ges.* xii. 458.

2301 *Acetyldioxindol*, $C_8H_6N(CO.CH_3)O_2$, is obtained by heating dioxindol to 140° with acetic anhydride; it crystallizes from hot water in short prisms, melting at 127°.[1]

Acetylorthamidomandelic acid or *Acetylhydridinic acid* $C_6H_4(NH.CO.CH_3)(CH.OH)CO_2H$, is formed when the preceding compound is dissolved in baryta water:



It is also obtained when an acetic acid solution of acetylisatic acid, $C_6H_4(NH.CO.CH_3)CO.CO_2H$, is treated with sodium amalgam.[2] It crystallizes in needles, which are readily soluble in water and alcohol, melt at 142°, and on further reduction by means of sodium amalgam or hydriodic acid and phosphorus, are resolved into acetic acid and oxindol.

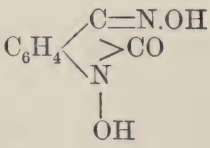
Nitrosodioxindol, $C_8H_6N(NO)O_2$, is prepared by the action of nitrous acid on an alcoholic solution of dioxindol, and crystallizes from hot water in yellow, moss-like groups of needles, which are very brittle, melt at 300°—310° and sublime at 340° in white needles.

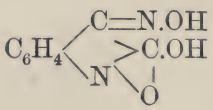
Ammonium nitrosodioxindol, $2\,C_6H_5(NH_4)(NO)NO_2 + H_2O$, crystallizes in silky plates, which are only very slightly soluble in water.

Barium nitrosodioxindol, $C_6H_4Ba(NO)NO_2$, is thrown down as a crystalline precipitate, when barium chloride is added to an aqueous solution of nitrosodioxindol; it is soluble in boiling water.

Silver nitrosodioxindol, $C_6H_4Ag_2(NO)NO_2$, is obtained by the addition of silver nitrate to the solution of the ammonium salt, in the form of a yellowish white precipitate.

Nitrosodioxindol contains two hydrogen atoms which can be replaced by metals and appears to be an isonitroso-compound, its constitution being expressed by one of the following formulæ:





[1] Suida, *Ber. Deutsch. Chem. Ges.* xii. 1326.

[2] *Ibid.* xi. 586.

Azodioxindol, $C_8H_6N_2O_2$, is formed when nitrosodioxindol is boiled with dilute caustic potash solution and ferrous sulphate, and crystallizes in lustrous, white, prismatic needles, which are slightly soluble in water, readily in caustic potash and boiling alcohol, sublime at 260° in lustrous, quadratic tablets and melt at 300°. *Silver azodioxindol*, $C_8H_4Ag_2N_2O_2$, is obtained as a white, crystalline precipitate by the addition of silver nitrate and then ammonia to a solution of this body.

Azoxindol, $2C_8H_6N_2O + H_2O$, is obtained when nitrosodioxindol is treated with a little water and sodium amalgam; it crystallizes from alcohol in cubes, which become anhydrous at 140° and sublime at 220° in plates, without previously melting. It contains one hydrogen atom which can be replaced by metals.

Substitution products of dioxindol have been prepared by Baeyer and Knop by the action of chlorine or bromine on its aqueous solution:

Chlorodioxindol, $C_8H_6ClNO_2$, yellowish needles.
Dichlorodioxindol, $C_8H_5Cl_2NO_2$, dirty green scales.
Bromodioxindol, $C_8H_6BrNO_2$, light yellow needles.
Dibromdioxindol, $C_8H_5Br_2NO_2$, dark red needles.

2302 *Orthohydroxymandelic acid*, $C_6H_4(OH)CH(OH)CO_2H$, was prepared by Plöschl, who named it *salicylglycolic acid*, by combining salicylaldehyde with hydrocyanic acid and decomposing the product with hydrochloric acid. It is also formed by the action of water and sodium amalgam on hydroxybenzoylformic acid,[1] and has hitherto only been obtained in the form of a syrup; it forms salts which are crystalline.[2]

Methylparahydroxymandelic acid, $C_6H_4(OCH_3)CH(OH)CO_2H$ The nitril of this acid is formed when anisaldehyde is heated with aqueous hydrocyanic acid, and is a crystalline substance, melting at 63°. The acid is obtained from it by heating with alcohol and hydrochloric acid; it crystallizes in ice-like masses, in which small needles can be distinguished, and melts at 93°.[3]

Methylenedihydroxymandelic acid, $CH_2\begin{smallmatrix}O\\O\end{smallmatrix}C_6H_3.CH(OH)CO_2H$. The nitril is formed by heating piperonal (Pt. IV. p. 347) with hydrocyanic acid. The acid, which is prepared from this

[1] Baeyer and Fritsch, *Ber. Deutsch. Chem. Ges.* xvii. 973.
[2] *Ibid.* xiv. 1317.
[3] Tiemann and Köhler, *ibid.* xiv. 1976.

by the usual method, forms granular crystals, melting at 152°—153°; it readily decomposes carbonates, but is very unstable and forms a resinous mass even when the aqueous solution is boiled.[1]

BENZOYLMETHYL COMPOUNDS.

Methylphenylketone, $CH_3.CO.C_6H_5$.

2303 This compound, which is usually known as *acetophenone* and is the simplest aromatic ketone, was first prepared by Friedel by the distillation of a mixture of calcium acetate and benzoate,[2] while Popow obtained it by the action of zinc methyl on benzoyl chloride.[3] It is also readily formed when a mixture of acetyl chloride and benzene is heated with aluminium chloride,[4] and, together with benzoic acid, when ethylbenzene is oxidized by a solution of chromium trioxide in glacial acetic acid.[5] In addition to these methods it may be obtained by agitating phenylacetylene with 75 per cent. sulphuric acid:[6]

$$C_6H_5.C{\equiv}CH + H_2O = C_6H_5.CO.CH_3.$$

When sodium aceto-acetic ether is acted upon by benzoyl chloride, benzoylaceto-acetic ether, $CH_3.CO.CH(CO.C_6H_5)CO_2.C_2H_5$, is formed, and decomposes on heating with water or alkalis into acetic acid, acetophenone, carbon dioxide and alcohol.[7] Acetophenone crystallizes in large plates, which melt at 20·5°;[8] it boils at 202°,[9] and has an aromatic odour resembling that of oil of bitter almonds. It is oxidized by chromic acid solution to benzoic acid (Popow) and is reduced by nascent hydrogen to methylphenyl carbinol; the pinacone, $C_{16}H_{18}O_2$, which will be subsequently described, is also formed in this reaction.

Its action upon the organism is similar to that of chloral, since doses of 0·05—0·15 grm. produce quiet sleep; Dujardin-

[1] Lorenz, *Ber. Deutsch. Chem. Ges.* xiv. 794.
[2] *Compt. Rend.* xlv. 1013.
[3] *Ber. Deutsch. Chem. Ges.* iv. 720.
[4] Friedel and Crafts, *Ann. Chim. Phys.* [6] i. 507.
[5] Friedel and Balsohn, *Bull. Soc. Chim.* xxxii. 616.
[6] *Ibid.* xxxv. 55.
[7] Bonné, *Ann. Chem. Pharm.* clxxxvii. 1.
[8] Städel and Kleinschmidt, *Ber. Deutsch. Chem. Ges.* xiii. 836.
[9] Fittig and Wurster, *Ann. Chem. Pharm.* cxcv. 160.

Beaumetz and Bardet have therefore called it *hypnone*.[1] It is converted in the system into hippuric acid, which is excreted with the urine. After long-continued use, however, a portion is excreted through the lungs and imparts its characteristic smell to the breath.

Acetophenone-acetoxime, $\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!C=N.OH$, crystallizes from hot water in silky needles, which melt at 59° and are extremely soluble in alcohol, ether, acetone, etc.[2]

Acetophenonephenylhydrazine, $\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>\!C=N_2H.C_6H_5$, crystallizes from hot alcohol in fine, white needles, melting at 105°.[3]

Parachloracetophenone, $C_6H_4Cl.CO.CH_3$, is obtained by heating chlorobenzene with acetyl chloride and aluminium chloride. It forms crystals, melting at 20°, boils at 230°—231°, smells like acetophenone, but somewhat sharper, and is oxidized by potassium permanganate to parachlorobenzoic acid.[4]

Para-iodo-acetophenone or *Acetyliodobenzene*, $C_6H_4I.CO.CH_3$, was prepared by Klinger from the amido-compound by the diazo-reaction. It crystallizes from ether in small plates or flat needles, melting at 79°, and yields para-iodobenzoic acid on oxidation.

Orthonitro-acetophenone, $CH_3.CO.C_6H_4.NO_2$, is formed, together with the meta-compound, by the nitration of acetophenone.[5] It may be obtained pure by acting upon sodiumaceto-acetic ether with orthonitrobenzoyl chloride and decomposing the ethyl benzoylaceto-acetate by boiling with dilute sulphuric acid.[6] It is a yellowish oil, which is volatile with steam and is oxidized to orthonitrobenzoic acid by potassium permanganate (Engler).

Metanitro-acetophenone has been prepared from metanitrobenzoyl chloride (Gevekoht); it is, however, more easily obtained by the nitration of the ketone, which yields this derivative alone when the mixture is well cooled.[7] It is volatile with steam and forms colourless needles, which melt at 81° and are converted by oxidation into metanitrobenzoic acid.

[1] *Compt. Rend.* ci. 960 and 1506; *Bull. Therap.* Jan. 15, 1886.
[2] Janny, *Ber. Deutsch. Chem. Ges.* xv. 2781.
[3] Reisenegger, *Ber. Deutsch. Chem. Ges.* xvi. 662.
[4] Gautier, *Bull. Soc. Chim.* xliii. 602.
[5] Emmerling and Engler, *ibid.* iii. 886; Engler, *ibid.* xviii. 2238.
[6] Gevekoht, *Ann. Chem. Pharm.* ccxxi. 323.
[7] Buchka, *Ber. Deutsch. Chem. Ges.* x. 1714.

Paranitro-acetophenone was obtained by Drewsen by boiling paranitrophenylpropiolic acid, $C_6H_4(NO_2)C \equiv C.CO_2H$, with sulphuric acid of 75 per cent.; this acid decomposes into carbon dioxide and paranitrophenylacetylene, which then combines with water to form the ketone.[1] Gevekoht subsequently prepared it from paranitrobenzoyl chloride. It crystallizes from hot water in yellowish prisms, melting at 80°—81°.

Orthamido-acetophenone, $CH_3.CO.C_6H_4.NH_2$, is formed by the reduction of the nitro-compound with tin and hydrochloric acid, as well as by the action of sulphuric acid of 75 per cent. on amidophenylacetylene,[2] $C_6H_4(NH_2)C \equiv CH$. It is a yellowish oil, which can be volatilized without decomposition, and yields a vapour with a penetrating odour, which adheres to the skin for a long time, while, when diluted with air, the odour loses its pungent character and becomes more agreeable. It forms salts with acids, and on boiling with acetic anhydride yields *acetorthamido-acetophenone*, $CH_3.CO.C_6H_4.NH(CO.CH_3)$, which crystallizes from petroleum-spirit in silky needles, melting at 76°—77°. The corresponding benzoyl derivative, *benzoylortho-amido-acetophenone*, $CH_3.CO.C_6H_4.NH(CO.C_6H_5)$, is formed by the action of benzoyl chloride; it crystallizes in large, yellowish prisms, and melts at 79°—80°. As a secondary base it forms a nitroso-compound, which crystallizes in long, colourless needles, melting at 54°—55°, and is decomposed on heating with sulphuric acid with formation of indigo.[3]

Ethylorthamido-acetophenone, $CH_3.CO.C_6H_4.NH(C_2H_5)$, is obtained by heating the amidoketone with ethyl bromide, as a yellowish oil, which possesses a very characteristic odour, quite distinct from that of the amido-acetophenone (Baeyer).

Metamido-acetophenone is formed by the action of tin,[4] or zinc,[5] and hydrochloric acid on the corresponding nitro-compound. It is soluble in alcohol and crystallizes in small, yellow pyramids, melting at 92°—93°. Its hydrochloride is partially decomposed by water.

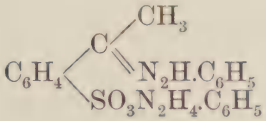
Paramido-acetophenone was obtained by Drewsen by the reduction of the nitro-derivative, and Klinger, who named it *acetylaniline*, found that it is also formed when two parts of aniline, three parts of zinc chloride, and five parts of acetic

[1] *Ann. Chem. Pharm.* ccxii. 159.
[2] Baeyer and Blöm, *Ber. Deutsch. Chem. Ges.* xv. 2153 ; xvii. 963.
[3] Baeyer, *ibid.* xvii. 970.
[4] Buchka, *loc. cit.* ; Engler, *Ber. Deutsch, Chem. Ges.* xi. 932.
[5] Hunnius, *ibid.* x. 2009.

anhydride are heated to the boiling-point for four to five hours.[1] It crystallizes from hot water in fan-shaped groups of long, flat needles, melting at 105°—106°, boils at 293°—295° without decomposition, and combines with acids to form salts which crystallize well. When heated with acetic anhydride it yields *acetorthamido-acetophenone*, which crystallizes from hot water in small needles, melting at 166°—167°.

Dimethylparamido-acetophenone, $CH_3.CO.C_6H_4.N(CH_3)_2$, is formed when paramido-acetophenone is heated with methyl iodide, and crystallizes from hot water in yellowish plates, melting at 58°—59°.

Acetophenonesulphonic acid, $CH_3.CO.C_6H_4.SO_3H$, is formed when acetophenone is heated for some time with concentrated sulphuric acid. The free sulphonic acid, which is prepared by the decomposition of its lead salt with sulphuretted hydrogen, is very hygroscopic and forms a compound of the following constitution with phenylhydrazine:



This crystallizes in nacreous plates and is resolved into phenylhydrazine and barium acetophenonesulphonate by boiling with baryta water.[2]

2304 *Parahydroxyacetophenone*, $CH_3.CO.C_6H_4OH$, which is also called *acetylphenol*, was prepared by Klinger by means of the diazo-reaction, while Michael and Palmer obtained it by heating phenol with glacial acetic acid and zinc chloride:

$$CH_3.CO.OH + C_6H_5.OH = CH_3.CO.C_6H_4.OH + H_2O.$$

It crystallizes from alcohol in long prismatic needles or short prisms, which are insoluble in water but dissolve in hot hydrochloric acid and melt at 108°.[3]

Paradihydroxyacetophenone, $CH_3.CO.C_6H_3(OH)_2$, or *Quinacetophenone*, is formed when two parts of quinol are heated to 140°—150° with three parts of glacial acetic acid and three parts of zinc chloride. It is readily soluble in alcohol and ether, crystallizes

[1] Hunnius, *Ber. Deutsch. Chem. Ges.* xviii. 2687.
[2] Krekeler, *ibid.* xix. 2623.
[3] *Amer. Chem. Journ.* vii. 277.

from hot water in yellowish green, dendritic forms, resembling those of sal-ammoniac, and melts at 202°. Its aqueous solution is coloured a fugitive deep blue by ferric chloride; it dissolves in alkalis with formation of a light yellow solution, which soon becomes brown in the air. Like quinol it reduces Fehling's solution.[1]

Metadihydroxyacetophenone or *Resacetophenone* is prepared from resorcinol in a similar manner to the preceding compound, and crystallizes from hot dilute hydrochloric acid in colourless rhombic plates or needles, melting at 142°. The dilute aqueous solution is coloured wine-red by ferric chloride. On heating with acetic anhydride, the monacetate, $CH_3.CO.C_6H_3(OH)O.C_2H_3O$, is formed, which crystallizes from alcohol in fine needles, melts at 72° and boils at 303°. All attempts to prepare the diacetate have proved unsuccessful.

Methylresacetophenone or *Paeonol*, $C_6H_3(OH)(OCH_3)CO.CH_3$, occurs to the extent of 3—4 per cent. in the aromatic root of *Paeonia mutan* from Japan, and volatilizes on distillation with steam in fine needles, melting at 47°.[2]

Nitroresacetophenone, $CH_3.CO.C_6H_2(NO_2)(OH)_2$, is formed by the action of ordinary nitric acid on the ketone and crystallizes from dilute alcohol in long, yellowish needles, melting at 142°.[3]

It is reduced to *amidoresacetophenone*, $CH_3.CO.C_6H_2(NH_2)(OH)_2$, by tin and hydrochloric acid; the hydrochloride of this substance crystallizes in lustrous prisms.[4]

Trihydroxyacetophenone or *Gallacetophenone*, $CH_3.CO.C_6H_2(OH)_3$, has been prepared by Nencki and Sieber from pyrogallol and acetic acid, and crystallizes from hot water in nacreous plates, melting at 168°. Its alkaline solution becomes coloured yellow and then brown in the air.

When these compounds are heated with zinc chloride and acetic acid, colouring matters which will be subsequently described are formed.

[1] Nencki and Schmid, *Journ. Prakt. Chem.* [2] xxiii. 556.
[2] W. Will. *Ber. Deutsch. Chem. Ges.* xix. 1776.
[3] Nencki and Sieber, *Journ. Prakt. Chem.* [2] xxiii. 147.
[4] *Ibid.* [3] xxiii. 537.

BENZOYLMETHYL ALCOHOL.
$C_6H_5CO.CH_2.OH$.

2305 This compound was first prepared by Graebe from the chloride and named *acetylbenzol alcohol*.[1] Hunaeus and Zincke then obtained *benzoylcarbinol* by the oxidation of styrolene alcohol with nitric acid,[2] and Hunnius, who named it *acetophenone alcohol*, prepared it from its bromide.[3]

Benzoylmethyl alcohol crystallizes from alcohol or ether in large, lustrous, six-sided tablets, which apparently belong to the monosymmetric system, and from petroleum-spirit in prisms or thick plates, melting at 85·5°—86°. It separates from water or dilute alcohol in large, lustrous, hydrated plates, which probably have the formula $C_6H_5C(OH)_2CH_2.OH$, melt at 73°—74° and on careful heating lose water, but are very liable to decompose with formation of benzaldehyde and a very volatile substance having a penetrating odour, which is probably formaldehyde.

As a ketone, benzoylmethyl alcohol combines with the acid sulphites of the alkalis, reduces ammoniacal silver solution and Fehling's solution, mandelic acid being the chief product, accompanied by benzaldehyde, benzoic acid and benzoylformic acid.[4] The reduction probably proceeds according to the following equation:

$$\begin{array}{l} C_6H_5 \\ | \\ C(OH)_2 \\ | \\ CH_2.OH \end{array} + O = \begin{array}{l} C_6H_5 \\ | \\ CH(OH) \\ | \\ CO.OH \end{array} + H_2O$$

Benzoylmethyl chloride, was prepared by Graebe by the action of chlorine on boiling acetophenone and was named by him *chloroacetylbenzol*. It was then investigated by Städel.[5] It is readily soluble in alcohol, ether, &c., and crystallizes in thick, rhombic tablets, which melt at 58°—59° and have an agreeable aromatic odour. It boils at 244°—245° and yields a vapour which produces a flow of tears.

Benzoylmethyl bromide, $C_6H_5.CO.CH_2Br$, was obtained by

[1] *Ber. Deutsch. Chem. Ges.* iv. 34.
[2] *Ibid.* x. 1486; Zincke, *Ann. Chem. Pharm.* ccxvi. 306.
[3] *Ber. Deutsch. Chem. Ges.* x. 2006.
[4] Breuer and Zincke, *ibid.* xiii. 635.
[5] *Ibid.* x. 1830.

Emmerling and Engler, who named it *bromacetophenone*, by the direct action of bromine on acetophenone.[1] In order to prepare it, one molecule of bromine is gradually added to a molecule of acetophenone dissolved in carbon disulphide (Hunnius), a current of dry carbon dioxide being simultaneously passed through the liquid to remove the hydrobromic acid and carbon disulphide (Städel and Kleinschmidt). It crystallizes from dilute alcohol in rhombic prisms and from ether in tablets, which are apparently isomorphous with those of the chloride,[2] and melt at 50°. Its vapour attacks the eyes violently.

Orthonitrobenzoylmethyl bromide, $C_6H_4(NO_2)CO.CH_2Br$, is formed when equal molecules of bromine and orthonitroacetophenone are brought together in glacial acetic acid solution. It crystallizes from petroleum-spirit in fine, concentrically-grouped needles, which melt at 55°—56°, have a bitter taste and an exceptionally violent action on the eyes.[3]

Benzoylmethyl acetate, $C_6H_5.CO.CH_2.O.C_2H_3O$, is formed by heating the chloride (Graebe), or bromide (Hunnius) with alcohol and potassium acetate, or the alcohol with acetic anhydride (Hunaeus and Zincke). It is readily soluble in alcohol, ether, and petroleum-spirit, from which it crystallizes in lustrous, rhombic tablets, melting at 49°—49·5°.

Benzoylmethyl benzoate, $C_6H_5.CO.CH_2.O.C_7H_5O$, crystallizes from hot alcohol in small tablets, which are frequently massed together in the form of flat needles, and melt at 117°—117·5°.

Benzoylmethyl phenyl ether, $C_6H_5.CO.CH_2.O.C_6H_5$, is obtained by boiling the bromide with an alkaline solution of phenol. It crystallizes from alcohol in prisms, melting at 72°, and is not decomposed by caustic soda solution. On fusion with caustic potash, however, it decomposes into phenol and acetophenone, which is then partially oxidized to benzoic acid.[4]

[1] *Ber. Deutsch. Chem. Ges.* iv. 148.
[2] Städel, *ibid.* xvi. 22. This chemist has proposed the name of *phenacyl* for the radical benzoylmethyl.
[3] Gevekoth, *Ann. Chem. Pharm.* ccxxi. 323.
[4] Möhlau, *Ber. Deutsch. Chem. Ges.* xv. 2497.

BENZOYLMETHYLENE-COMPOUNDS.

2306 These are formed by the replacement of two hydrogen atoms in the methyl group of acetophenone.

Benzoylmethylene chloride, $C_6H_5.CO.CHCl_2$, is formed when aluminium chloride is gradually added to a boiling mixture of benzene and dichloracetaldehyde, and is a liquid which smells like pepper, has a biting taste and boils at 247°—248° with slight decomposition.[1]

Benzoylmethylene bromide, $C_6H_5.CO.CHBr_2$. This compound, which is usually called *dibromacetophenone*, is best obtained by gradually adding the calculated quantity of bromine to acetophenone dissolved in glacial acetic acid, then heating to 65°-70° and pouring the solution into cold water. The product is purified by recrystallization from petroleum-spirit.[2] It forms rhombic tablets (Fittig and Wurster) which melt at 36°-37°. Potassium permanganate oxidizes it to benzoic acid (Hunnius), while ammonia decomposes one portion into benzamide and methylene bromide, while the remainder is converted into *iso-indileucin* $C_{16}H_{12}N_2O$, which will be subsequently described.

Orthonitrobenzoylmethylene bromide, $C_6H_4(NO_2).CO.CHBr_2$, was prepared by Gevekoth by the bromination of orthonitro-acetophenone. It crystallizes from petroleum-ether in small prisms, melting at 85°-86°, has a bitter taste, causes a copious flow of tears and, like orthonitrobenzoylmethyl bromide, is converted into indigo by the action of alcoholic ammonium sulphide.

Metanitrobenzoylmethylene bromide is formed by the nitration of the dibromide and by the bromination of metanitrobenzoylmethyl bromide. It crystallizes from alcohol in yellowish tablets, melting at 59° (Engler and Hassenkamp).

2307 *Iso-indol*, $C_{16}H_{14}N_2$, is obtained by boiling benzoylmethyl chloride with aqueous ammonia[3] or the acetate with alcoholic ammonia. It is, however, best prepared by allowing the bromide to stand in contact with the latter reagent in the cold:[4]

$$2C_6H_5CO.CH_2Br + 2NH_3 = C_{16}H_{14}N_2 + 2H_2O + 2HBr.$$

[1] Gautier, *Compt. Rend.* cii. 812.
[2] Engler and Hassenkamp. *ibid.* xviii. 2240.
[3] Städel and Rügheimer, *Ber. Deutsch. Chem. Ges.* ix. 563; Städel, *ibid.* x. Städel and Kleinschmidt, *ibid.* xi. 1744.
[4] *Ibid.* xiii. 836.

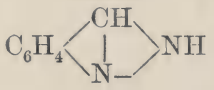
It is only slightly soluble in the usual solvents, and crystallizes from hot alcohol or glacial acetic acid in small plates, needles or prisms, which are pleochroitic and show all possible colours, from the deepest red, green, yellowish green, yellow to indigo-blue; larger crystals viewed by transmitted light often show this complete series of colours when they are rotated about their axes. It melts at 194°-195°, dissolves in hot concentrated hydrochloric acid and is reprecipitated by the addition of water. It sublimes when fused with potash or heated with lime, and is not attacked by heating with ethyl iodide, acetyl chloride or acetic anhydride; hydriodic acid, however, converts it into a base melting at 125°.

The name of iso-indol was given to this substance because it was believed to be isomeric with indol, C_8H_7N, (p. 36), until V. Meyer and Treadwell found that its formula must be doubled, since its vapour density is 7·91-7·99.[1]

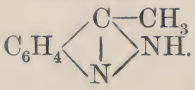
Phenylisoindol, $C_{16}H_{12}(C_6H_5)_2N_2$, is formed by boiling benzoyl-methyl bromide with an excess of aniline. It is readily soluble in the usual solvents, and crystallizes from carbon disulphide in lustrous plates, which melt at 181° and sublime readily. It is also not attacked by fused caustic soda or heated lime. Its vapour density is 13·33, and it should therefore be called *diphenyldi-iso-indol*.[2]

THE INDAZOL GROUP.

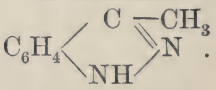
Indazol.



Methindazol.



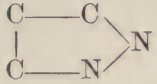
Methisindazol.



2308 Indazol, which contains seven carbon atoms, is described here along with its homologues, since these bodies are obtained by simple reactions from orthamido-acetophenone. E. Fischer, who has investigated these compounds in conjunction with Kuzel [3] and Tafel,[4] names the two last methylindazol and methyl-isindazol. In order to distinguish the derivatives which are

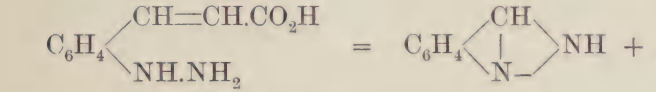
[1] *Ber. Deutsch. Chem. Ges.* xvi. 342.
[2] Möhlau, *ibid.* xiv. 173; xv. 2480.
[3] *Ann. Chem. Pharm.* ccxxi. 261.
[4] *Ibid.* ccxxvii. 303.

formed by replacing the imido-hydrogen by alcohol radicals, he designates the "five-atom nitrogen ring":



with the symbol Iz, and numbers the positions in rotation, commencing at the nitrogen atom which is combined with the benzene nucleus. Ethylindazol is therefore distinguished as Iz-2-ethylindazol, and methindazol as Iz-3-methylindazol while ethylmethisindazol receives the name of Iz-1-ethyl-Iz-3-methylisindazol.

Indazol, $C_7H_6N_2$, which has received this name on account of its relation to indol, C_8H_7N, is formed, together with acetic acid, when orthohydrazinecinnamic acid is heated:



It is readily soluble in alcohol and hot water, and crystallizes in fine needles, which melt at 146·5° but sublime rapidly at 100°; when heated it forms a vapour which has a sweet odour, resembling that of resorcinol. It boils at 269°-270°, and separates on the evaporation of its ethereal solution in large, well-formed crystals. It combines with acids to form salts, which are decomposed by water, and forms crystalline compounds with silver nitrate and mercuric chloride.

Ethylindazol, $C_7H_5N_2C_2H_5$, is formed by heating indazol with ethyl iodide, and is a brownish oily liquid, which smells like indazol and forms more stable salts.

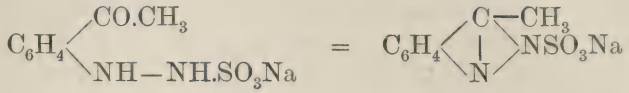
Nitroso-indazol, $C_7H_5N_2(NO)$ is obtained by the addition of sodium nitrite to a faintly acid, well-cooled solution of indazol, in the form of small, yellow needles, which crystallize from hot petroleum-spirit in golden-yellow, pointed needles, melting at 73°-74°.

Bromindazol, $C_7H_5BrN_2$, is prepared by heating bromindazolarboxylic acid, $C_7H_4BrN_2(CO_2H)$ with water to 200°. It crystallizes from hot water in long, thin needles, which melt at 124°.

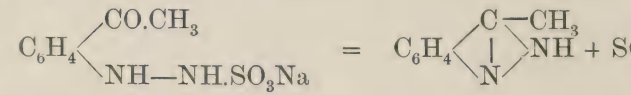
Dibromindazol, $C_7H_4Br_2N_2$, is formed by the action of bromine-water on indazol, bromindazol and bromindazolcarboxylic acid. This last method of formation renders it probable that one atom of bromine is contained in the side chain. It is insoluble in

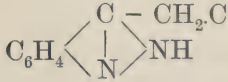
water, but dissolves readily in alcohol, &c., and crystallizes in needles, which melt at 239°-240° and sublime at a slightly higher temperature.

2309 *Methindazol*, $C_8H_8N_2$ is formed when orthamido-acetophenone is converted into a diazo-salt and treated in solution with sodium sulphite; *sodium hydrazine-acetophenonesulphonate* is formed and rapidly changes into *sodium methindazolsulphonate*, which separates in lustrous plates:



Both these salts are decomposed by hydrochloric acid with formation of methindazol:



It is also formed by heating *indazolacetic acid*,  , which will be subsequently described.

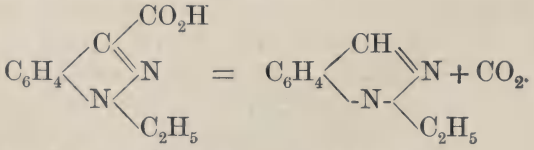
It is readily soluble in alcohol, tolerably in hot water, from which it crystallizes in long, thin needles, which rapidly become coloured red, melt at 113° and readily sublime. It boils at 280°—281°, and has a similar smell to indazol; its salts are more stable than those of the latter, and it also combines with silver nitrate and mercuric chloride.

Methylmethindazol, $C_8H_7N_2CH_3$, is formed by heating methindazol with methyl iodide, and crystallizes in small plates melting at 79°—80°.

Ethylmethindazol, $C_8H_7N_2C_2H_5$, is an oily liquid, volatile with steam, and possesses an odour resembling that of quinoline.

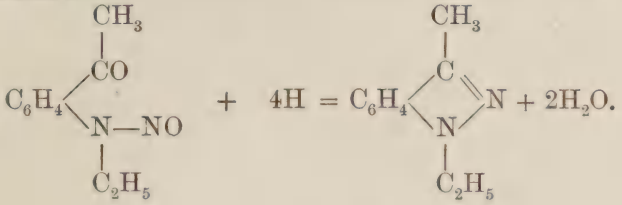
Nitrosomethindazol, $C_8H_7N_2(NO)$, crystallizes from petroleum-spirit in yellow needles, melting at 60·5°.

Ethylbromisindazol, $C_9H_9BrN_2$, is formed by the distillation of ethylbromisindazolcarboxylic acid:



It forms a soft, crystalline mass, melting at 48°.

Ethylmethisindazol, $C_{10}H_{12}N_2$, was first prepared by heating ethylisindazolacetic acid, $C_7H_4N_2(C_2H_5)CH_2.CO_2H$, and then from orthamido-acetophenone, which is converted into ethylamido-acetophenone by heating with ethyl iodide, the nitrosamine of which yields the base on reduction with zinc dust and acetic acid :



Ethylmethisindazol boils at 234°—235°, and solidifies on cooling in plates which melt at 30°, have a pungent taste and are volatile with steam, forming a vapour which has a sharp, penetrating odour. Its salts are readily soluble and are decomposed by a large amount of water. As a tertiary base, it does not form a nitrosamine, but combines with methyl iodide to form the salt, $C_{10}H_{12}N_2CH_3I$, which crystallizes in strongly refractive needles.

Methylmethisindazol, $C_8H_7N_2CH_3$, has been prepared from methylamido-acetophenone: it is very similar to the ethyl compound and melts at 36·5°.

BENZOYL-FORMYL COMPOUNDS.

2310 *Benzoylformic acid*, $C_6H_5.CO.CO_2H$. The nitril of this acid was obtained by Liebig and Wöhler by the distillation of benzoyl chloride with mercuric cyanide, and named *cyanbenzoyl*,[1] $C_6H_5.CO.CN$. They found that on heating with caustic potash solution it is decomposed into potassium cyanide and potassium benzoate. Kolbe, however, thought that the corresponding acid might also be formed, and, at his suggestion, Strecker investigated the reaction in this direction but only succeeded in obtaining hydrocyanic and benzoic acids.[2] These products were also observed by Claisen, who effected the decomposition by heating with hydrochloric acid. When he allowed the mixture

[1] *Ann. Chem. Pharm.* iii. 267.
[2] *Ibid.* xc. 62.

to stand in the cold, however, he obtained benzoylformic acid.[1]

This compound, which is also known as *phenylglyoxylic acid*, is also formed by the oxidation of benzoylcarbinol and mandelic acid with dilute nitric acid[2] or potassium permanganate,[3] and its ethyl ether may be prepared by heating ethyloxalyl chloride with mercury phenyl:[4]

$$Hg\begin{<}C_6H_5\\C_6H_5\end{>} + \begin{matrix}COCl\\|\\CO.OC_2H_5\end{matrix} = Hg\begin{<}Cl\\C_6H_5\end{>} + \begin{matrix}CO.C_6H_5\\|\\CO.OC_2H_5\end{matrix}$$

Benzoylformic acid is very readily soluble in water, from which it is extracted by ether. On evaporation it remains as a thick, oily liquid, and it is separated by acids from concentrated solutions of its salts in this form. This liquid, which probably has the constitution $C_6H_5.C(OH)_2.CO_2H$, similarly to glyoxylic and mesoxalic acids, solidifies in a desiccator to a radiating or prismatic crystalline mass, which melts at 65°—66°, and decomposes on distillation into carbon monoxide and benzoic acid, a small quantity, however, being resolved into carbon dioxide and benzaldehyde. It is converted by sodium amalgam and water into mandelic acid, and by hydriodic acid and amorphous phosphorus into phenylacetic acid. It is only gradually converted into benzoic acid by boiling dilute nitric acid. When sulphuric acid is added to its solution in benzene, which contains thiophene, a deep red colouration, which soon passes into a deep bluish-violet, is produced. On the addition of water, the substance which has been formed dissolves in the benzene with a carmine red colour. The ethers, amide and nitril of the acid give the same reaction.[5]

When the acid is brought into contact with phenylhydrazine in dilute hydrochloric acid solution, *phenylhydrazinebenzoylformic acid*, $C_6H_5(CN_2H.C_6H_5)CO_2H$, separates as a yellow, voluminous precipitate. The acid can be easily detected by means of this reaction, even in very dilute solutions.[6]

Most of the salts of benzoylformic acid crystallize well and

[1] *Ber. Deutsch. Chem. Ges.* x. 429; Hübner and Buchka, *ibid.* x. 479; Buchka, *ibid.* xx. 395.
[2] Hunaeus and Zincke, *ibid.* x. 1486.
[3] Meyer and Baur, *Ann. Chem. Pharm.*, ccxx. 37.
[4] Claisen and Morley, *Ber. Deutsch. Chem. Ges.* xi. 1596.
[5] Claisen, *ibid.* xii. 1505.
[6] Elbers, *Ann. Chem. Pharm.* ccxxvii. 340.

are soluble in water, the least soluble being the barium, lead, silver and mercurous compounds.

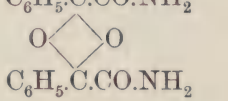
The ethers are best prepared by dissolving the nitril in the corresponding alcohol and saturating the solution, which must be cooled by a freezing mixture, with hydrochloric acid. They are pleasant smelling liquids, which, as ketones, form crystalline compounds with acid sodium sulphite.[1]

	Boiling-point.
Methyl benzoylformate, $C_6H_5.CO.CO_2.CH_3$ . .	246°—248°
Ethyl benzoylformate, $C_6H_5.CO.CO_2.C_2H_5$ . .	256°—257°

The homologues can only be distilled without decomposition under diminished pressure.

Benzoylformamide, $C_6H_5.CO.CO.NH_2$, is formed, together with the acid, by the action of concentrated hydrochloric acid on the nitril, and crystallizes from hot water in plates, which resemble those of benzoic acid, or in flat prisms, which melt at 90°—91° and distil almost without decomposition. It is readily soluble in alcohol, ether and dilute alkalis, from the last of which it is precipitated as the hydrate, $C_6H_5.CO.CO.NH_2 + H_2O$, which crystallizes in clear, lustrous, microscopic, quadratic prisms, which are almost insoluble in ether and cold water, and lose water and melt at 64°—65°. It crystallizes from tolerably hot water without change, but the anhydrous compound is deposited from a solution in boiling water, and is also obtained by the evaporation of the alcoholic solution. This hydrate has probably the constitution $C_6H_5.C(OH)_2CO.NH_2$.

When an alkaline solution of benzoylformamide is slowly run into an excess of hydrochloric acid, an isomeric, or more probably polymeric, compound separates out as a powder, which crystallizes from alcohol in prisms, which melt at 134°—135°, but after being kept at this temperature for a short time do not solidify until the temperature has fallen to 90°—80°, the normal compound being reproduced; it is also converted into the normal compound by boiling with water. The constitution of this substance is perhaps represented by the following formula:[2]



[1] *Ber. Deutsch. Chem. Ges.* xii. 626.
[2] Claisen, *ibid.* x. 1498; xii. 632.

It may also, however, be similar to that of paraldehyde (Part I., p. 479).

Isonitrosophenylacetic acid, $C_6H_5.C(N.OH)CO_2H$, is formed by the action of hydroxylamine on benzoylformic acid, and is a crystalline mass which is readily soluble in water, alcohol and ether, has an aromatic odour and melts at 127°—128°. It is converted into amidophenylacetic acid by tin and hydrochloric acid.[1]

Ethyl isonitrosophenylacetate, $C_6H_5.C(NOH)CO.OC_2H_5$, is obtained by the action of hydroxylamine on ethyl benzoylformate, and crystallizes from boiling water in long, lustrous needles, melting at 112°—113°.[2]

2311 *Benzoylformonitril*, $C_6H_5.CO.CN$, is prepared, as already mentioned, by the distillation of benzoyl chloride with mercuric cyanide. In order to free it from the latter, it is washed with warm water until a portion of the washings does not give a black colouration with sulphuretted hydrogen. Wöhler and Liebig described it as a liquid possessing a penetrating odour resembling that of oil of cinnamon, but producing a flow of tears, and having a sharp but sweet taste, with an after taste like that of hydrocyanic acid. Strecker found, however, that it solidifies after some time [3] and forms splendid, long, transparent asymmetric prisms,[4] melting at 33°—34°.

By the action of zinc and hydrochloric acid it is converted into benzaldehyde and hydrocyanic acid.[5] Alkalis decompose it into the latter and benzoic acid, while hydroxylamine converts it into dibenzhydroxamic acid (Part IV., p. 209). In these reactions, therefore, it behaves in an exactly analogous manner to benzoyl chloride (Müller). When its ethereal solution is treated with zinc ethide, benzoic acid, ethylphenylketone $C_2H_5.CO.C_6H_5$, and zinc cyanide are formed, together with a small quantity of *benzocyanidin*, $C_{24}H_{19}NO_2$, which crystallizes from alcohol in colourless needles, melting at 123°—124°.[6]

Phenyldichloracetic acid, $C_6H_5.CCl_2.CO_2H$, is formed by the action of chlorine on phenylchloracetic acid in the sunlight,[7] and its ethyl ether is obtained by treating ethyl benzoylformate with phosphorous chloride. This is readily saponified by

[1] Müller, *Ber. Deutsch. Chem. Ges.* xvi. 1617.
[2] Gabriel, *ibid.* xvi. 517.
[3] *Ann. Chem. Pharm.* xc. 62.
[4] Bodewig, *Ber. Deutsch. Chem. Ges.* xii. 626.
[5] Kolbe, *Ann. Chem. Pharm.* xcviii. 344.
[6] Frankland and Louis, *Journ. Chem. Soc.* 1880, i. 742.
[7] Radziszewski, *Ber. Deutsch. Chem. Ges.* ii. 209.

alcoholic potash, the potassium salt, which crystallizes in prisms and is very soluble in water and alcohol, being formed. The free acid is liberated by the addition of hydrochloric acid to an aqueous solution of this salt, and remains, after extraction with ether and evaporation of the latter, as a thick, oily liquid, which solidifies after standing for some time in a desiccator, to small, very deliquescent tablets or cubes.[1]

Ethyl phenyldichloracetate, $C_6H_5.CCl_2.CO_2.C_2H_5$, is a heavy, pleasant smelling liquid, which boils at 263°—266°.

Phenyldichloracetonitril, $C_6H_5.CCl_2.CN$, is formed by the action of phosphorous chloride on benzoylformonitril, and is a transparent colourless liquid, which has a characteristic odour, boils at 223°—224°, and is decomposed by caustic potash into potassium benzoate, cyanide and chloride.[2]

Metanitrobenzoylformic acid, $C_6H_4(NO_2)CO.CO_2H$, is prepared from the corresponding amide by heating it in tolerably dilute alkaline solution on the water bath until all smell of ammonia has disappeared. The solution is then acidified with nitric acid and extracted with ether, the acid being left on the evaporation of the latter as a yellowish, viscid syrup, which solidifies in a desiccator to small, short prisms. It melts at 77°—78°, is readily soluble in water, alcohol and ether, has a very bitter taste, which also characterizes its salts, and gives the same reaction as benzoylformic acid with sulphuric acid and benzene containing thiophene.[3]

Metanitrobenzoylformamide, $C_6H_4(NO_2)CO.CO.NH_2$, is formed, together with a large amount of metanitrobenzoic acid, when a mixture of equal parts of benzoylformamide and potassium nitrate is brought into ten parts of sulphuric acid at — 10°,[4] and may also be obtained by the action of the most concentrated cold hydrochloric acid on the nitril. It is scarcely soluble in cold, more readily in boiling water, from which it crystallizes in white or yellowish, narrow prisms, which melt at 151°—152°.

Metanitrobenzoylformonitril, $C_6H_4(NO_2)CO.CN$, is best prepared by the distillation of metanitrobenzoyl chloride with mercuric cyanide under diminished pressure (Claisen and Thompson). It is also formed in small quantity, together with a large amount of metanitrobenzoic acid, when a mixture

[1] Claisen, *Ber. Deutsch. Chem. Ges.* xii. 630.
[2] *Ibid.* xii. 626.
[3] Claisen and Thompson, *ibid.* xii. 1942.
[4] Thompson, *ibid.* xiv. 1185.

of benzoylformonitril and potassium nitrate is brought into well-cooled sulphuric acid (Thompson), and is a thick, light yellow liquid, which has a faint odour resembling that of benzoylformonitril, boils at 230°—231·5° under a pressure of 142—147 mm. and does not solidify at — 17°. It dissolves in concentrated caustic potash solution with formation of hydrocyanic acid and metanitrobenzoic acid.

Orthonitrobenzoylformic acid, $C_6H_4(NO_2)CO.CO_2H$, is prepared from its amide in a similar manner to the meta-acid. It separates from an alkaline solution on the addition of hydrochloric acid as a pale yellow oil, which soon solidifies. It dissolves in every portion in tolerably hot water and crystallizes on cooling, frequently only after standing for some time, in long, hair-like, lustrous prisms, which probably have the formula, $C_6H_4(NO_2)C(OH)_2CO_2H$, and melt at 46°—47°. They lose water over sulphuric water and then melt with decomposition at 122°—123°.[1]

Orthonitrobenzoylformamide, $C_6H_4(NO_2)CO.CO.NH_2$, is formed by the action of cold, fuming hydrochloric acid on the nitril, and crystallizes from hot water in small, white prisms, melting at 189°.

Orthonitrobenzoylformonitril, $C_6H_4(NO_2)CO.CN$, is obtained by heating orthonitrobenzoyl chloride with silver cyanide to 100°, and crystallizes from hot petroleum-spirit in white, strongly lustrous prisms, melting at 54°.[2]

Orthohydroxybenzoylformic acid, $C_6H_4(OH)CO.CO_2H$, has been prepared from isatic acid (p. 77) by means of the diazo-reaction. It crystallizes from a mixture of benzene and petroleum spirit in concentric groups of needles, melting at 43°—44°, and is converted into orthohydroxymandelic acid by water and sodium amalgam.[3]

Veratroylcarboxylic acid, $C_6H_3(OCH_3)_2CO.CO_2H$, is formed, together with veratric acid (Part IV., p. 354) by the oxidation of methyleugenol, $C_6H_3(OCH_3)_2C_3H_5$, with potassium permanganate. It dissolves very readily in water and alcohol, and crystallizes from anhydrous benzene in fine needles, melting at 138°—139°, while in the presence of water, transparent tablets are formed, which effloresce in the air. It is converted into veratric acid by further oxidation, and into protocatechuic acid by fusion with potash.[4]

[1] Claisen and Shadwell, *Ber. Deutsch. Chem. Ges.* xii. 1945.
[2] *Ibid.* xii. 350.
[3] Baeyer and Fritsch, *ibid.* xvii. 973.
[4] Tiemann and Matsmoto, *ibid.* xi. 141.

Metamidobenzoylformic acid, $C_6H_4(NH_2)CO.CO_2H$, is prepared by the reduction of the nitro-acid with ferrous sulphate in alkaline solution. It is only slightly soluble in cold water and crystallizes from boiling water in strongly lustrous needles or prisms, which are almost insoluble in alcohol and ether, and decompose on heating. The hydrochloride crystallizes in concentrically grouped, flat prisms. This acid also gives the characteristic reaction with sulphuric acid and benzene containing thiophene (Claisen and Thompson).

ISATIN, $C_8H_5NO_2$.

2312 This compound, the name of which is derived from *Isatis tinctoria*, the woad or European indigo plant, was simultaneously discovered by Erdmann and Laurent in 1841. The former prepared it by heating indigo-blue, $C_{16}H_{10}N_2O_2$, with a dilute solution of chromic acid,[1] and the latter showed that nitric acid can be employed as the oxidizing agent.[2] They also found that it is converted by the action of alkalis into *isatic acid*, $C_8H_7NO_3$, and that on treatment with chlorine and bromine it yields substitution-products which had been previously prepared by Erdmann from indigo.[3]

Hofmann then observed that isatin is converted into aniline by fusion with caustic potash:

$$C_8H_5NO_2 + 4KOH = C_6H_7N + 2K_2CO_3 + H_2.$$

In this way he prepared the substituted anilines from the substitution-products of isatin, the discovery of these being of the greatest importance for the development of the theory of substitution (Part I., p. 15). He also found that dilute nitric acid oxidizes isatin to nitro-salicylic acid, which had previously been prepared from indigo (Part IV., p. 315), and subsequently showed that this substance is also formed when isatin is suspended in water and treated with nitrous acid,[4] whilst benzoic acid is formed in the presence of alcohol.[5] It followed from these facts that the nitrogen atom in isatin is directly combined

[1] *Journ. Prakt. Chem.* xxiv. 10.
[2] *Ann. Chim. Phys.* [3] iii. 372.
[3] *Journ. Prakt. Chem.* xix. 320.
[4] *Ann. Chem. Pharm.* cxv. 280.
[5] Baeyer and Knopp, *ibid.* cxl. 1.

with a carbon atom of the benzene nucleus, but no further conclusions as to the constitution of this substance could be drawn. The study of its reduction-products, which was carried out by Laurent, and subsequently by Schützenberger, was also fruitless of results in this direction, since the composition of these products is more complicated than that of isatin itself.

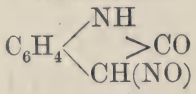
Baeyer and Knop, however, were more successful and their investigations led to the determination of the constitution both of isatin and indigo. By the addition of hydrogen and the successive removal of the two atoms of oxygen they prepared the following compounds, which have already been described :

Isatin	$C_8H_5NO_2$
Dioxindol	$C_8H_7NO_2$
Oxindol	C_8H_7NO
Indol	C_8H_7N.

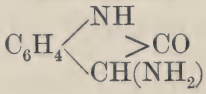
Baeyer then found that oxindol is the anhydride of orthamido-phenylacetic acid.

In conjunction with Knop, he had previously prepared a compound by the action of nitrous acid on oxindol, which they considered to be nitroso-oxindol, but which subsequently proved to be the isonitroso-derivative of isatin. By the reduction of this, Baeyer obtained amido-oxindol, which was converted into isatin by oxidation. He assigned the following formulæ to these compounds : [1]

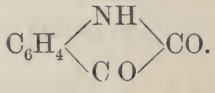
Nitroso-oxindol.



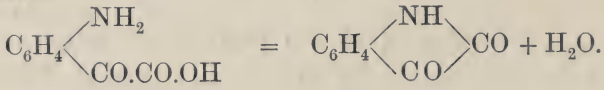
Amido-oxindol.



Isatin.



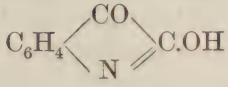
Kekulé had previously, in 1869, proposed this formula for isatin,[2] and it was confirmed in 1879 by the researches of Claisen and Shadwell, who found that orthamidobenzoylformic acid is identical with isatic acid, isatin being, therefore, its anhydride.[3]



It followed from this that oxindol, dioxindol and isatin are the anhydrides, or, as Baeyer terms them, the *lactams* of orthamido-

[1] *Ber. Deutsch. Chem. Ges.* xi. 1228. [2] *Ibid.* ii. 748. [3] *Ibid.* xii. 350.

acids. An extended series of investigations, however, has led him to the view that isatin does not contain the imido-group but the hydroxyl-group, its constitution being expressed by the following formula :[1]



It is therefore the *lactim* of isatic acid, orthamidobenzoylformic acid ; its lactam, which Baeyer names *pseudoisatin*, is not known in the free state, although some of its derivatives have been prepared.

He gives the general name of pseudo-compounds to compounds which do not exist in the free state, but immediately pass into an isomeric, stable form.[2]

It may here be mentioned that Blyth and Hofmann had endeavoured in 1845 to convert styrolene into isatin. They hoped to obtain the base, C_8H_9N, by the reduction of nitrostyrolene (p. 35), and expected that this would yield compounds of the indigo series on oxidation, among which isatin might occur ; their experiments, however, proved unsuccessful.[3]

Various methods of procedure have been proposed for the preparation of isatin from indigo.

According to Knop, 500 grms. of very finely powdered indigo are heated to boiling with 1·5 litres of water in an evaporating basin of 10 litres capacity, since the reaction causes considerable frothing, and to this the necessary amount of nitric acid, of sp. gr. 1·35, is added as rapidly as the frothing will allow. When the indigo contains 45 per cent. of colouring matter, 320 grms. of acid must be employed, 350 grms. if the indigo contain 50 per cent., &c.[4]

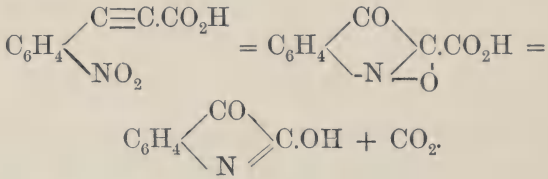
According to Sommaruga, 50 grms. of good indigo, containing 60—70 per cent. of the colouring matter, are ground as fine as possible and stirred with water to a thin paste, which is then heated to boiling and treated gradually with a concentrated solution of 30 grms. of chromium trioxide. The boiling is continued until the light foam has disappeared and large bubbles appear on the surface of the liquid. When everything has been previously prepared, four operations can be conducted simul-

[1] *Ber. Deutsch. Chem. Ges.* xv. 2100.
[2] *Ibid.* xix. 162 ; see also vol. iii. part iv. p. 518.
[3] *Ann. Chem. Pharm.* liii. 301.
[4] *Journ. Prakt. Chem.* xcvii. 86.

taneously and completed in ten minutes. The boiling solutions are then filtered and deposit the isatin, accompanied by a little brown resin, on cooling. The chromium sesquioxide, which remains in the filter, is extracted two or three times with boiling water and the extracts added to the mother-liquors, which are then either concentrated, a somewhat impure isatin being thus obtained, or extracted with ether after partial evaporation, isatin being taken up by ether from an aqueous solution, although in the solid state it is quite insoluble.[1]

The crude isatin is then purified by Hofmann's method,[2] according to which it is dissolved in cold caustic potash and the solution treated with hydrochloric acid as long as a dark-coloured precipitate is formed. As soon as a small portion of the filtered liquid appears of a pure yellow colour and gives a bright red precipitate on the further addition of hydrochloric acid, the resin is filtered off and the isatin completely precipitated, filtered and washed with a little water. The yield amounts to about 16—18 per cent. of the indigo-blue employed.

Isatin is also obtained when orthonitrophenylpropiolic acid, which is manufactured on the large scale, is boiled with alkalis, and this reaction takes place so readily and with so good a yield that Baeyer considers it to be the best method of preparation.[3] It is also formed when a solution of orthonitrophenylpropiolic acid in sulphuric acid is poured into water. The isomeric isatogenic acid is first formed, but immediately decomposes into isatin and carbon dioxide:[4]



Properties.—Isatin is slightly soluble in cold, readily in boiling water, forming a yellowish red solution, and also dissolves freely in hot alcohol; it crystallizes in dark red, monosymmetric prisms, or, when rapidly deposited, in small, yellowish red, lustrous needles, which melt at 200°—201°[5] and partially sublime when carefully heated. It imparts an unpleasant, adhering smell to the skin.

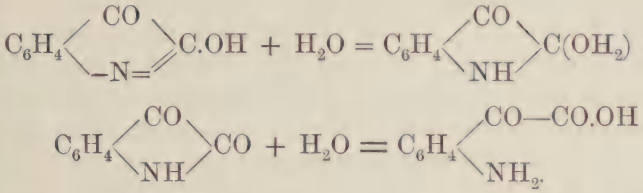
[1] *Ann. Chem. Pharm.* exc. 367.
[2] *Ibid.* liii. 11.
[3] *Ber. Deutsch. Chem. Ges.* xiii. 2259; see also Forrer, *ibid.* xvii. 976.
[4] Baeyer, *ibid.* xiv. 1741.
[5] Baeyer, *ibid.* xv. 2094.

When a solution of isatin in sulphuric acid is shaken up with benzene, which contains thiophene, a deep blue solution is formed (Part IV., p. 75), from which water precipitates *indophenin*, $C_{13}H_7NOS$, as a blue powder.[1]

A blue colouring matter, similar to indigo, is also formed when pyrrol and dilute sulphuric acid are added to an aqueous solution of isatin, or when pyrrol alone is added to a boiling solution of isatin in glacial acetic acid.[2]

Isatin dissolves in caustic potash and ammonia forming a dark red solution; on the addition of silver nitrate, a dark red precipitate of silver isatin, $C_8H_4AgNO_2$, is obtained.[3] When alcoholic solutions of isatin and silver nitrate, both containing ammonia, are mixed, a crystalline precipitate of $C_8H_4(NH_3Ag)NO_2$, of the colour of wine lees, is formed (Laurent).

2313 *Isatic acid* or *Orthamidobenzoylformic acid*, $C_6H_4(NH_2)CO.CO_2H$, is formed, according to Erdmann and Laurent, by heating an alkaline solution of isatin, the red colour of the solution changing to yellow. Baeyer explains this change by assuming that the lactim is first converted into the lactam:



Claisen and Shadwell, as previously mentioned, obtained this acid by reducing orthonitrobenzoylformic acid in alkaline solution with ferrous sulphate. It is left after the evaporation of its solution in vacuum as a white, indistinct crystalline powder. Its aqueous solution becomes coloured brownish-yellow on warming and then deposits isatin. Its salts are more stable, the potassium salt forming light yellow crystals.

Barium isatate, $(C_8H_6NO_3)_2Ba$, crystallizes in short, colourless prisms, which are only slightly soluble in water.

Silver isatate, $C_8H_6NO_3Ag$, separates in yellow prisms when hot solutions of the potassium salt and silver nitrate are mixed.

Isatinsulphurous acid is not known in the free state; its salts

[1] Baeyer and Lazarus, *Ber. Deutsch. Chem. Ges.* xviii. 2637.

[2] V. Meyer, *ibid.* xvi. 1478; Ciamician and Silber, *ibid.* xvii. 142; Meyer and Stadler, *ibid.* xvii. 1034.

[3] Laurent, *Journ. Prakt. Chem.* xxxv. 108; Baeyer, *Ber. Deutsch. Chem. Ges.* xv. 2093.

are formed by boiling isatin with the acid alkali sulphites, with which, like all other ketones, it combines.

Potassium isatinsulphite, $C_8H_5NO_2.SO_3KH+2H_2O$, is also formed when a solution of potassium isatate is saturated with sulphur dioxide and evaporated. It crystallizes in pale yellow tablets, which are only slightly soluble in water and are slowly decomposed by hydrochloric acid in the cold, but rapidly on heating.

2314 *Chlorisatin*, $C_8H_4ClNO_2$, is formed when chlorine is allowed to act upon indigo or isatin suspended in water (Erdmann, Laurent). It is best obtained by suspending isatin in boiling water and passing in chlorine, in the sunlight, until the crystals have assumed a pure orange-yellow colour. In this way, as Erdmann had previously stated, the product is obtained quite free from dichlorisatin (Hofmann), while, according to Dorsch, both substitution products are formed.[1]

Chlorisatin crystallizes in small, lustrous plates or transparent orange-yellow prisms, isomorphous with those of isatin, which dissolve in 200 parts of water at 100° and about 1,100 parts at 0°, and in 220 parts of alcohol of sp. gr. 0·830 at 14°. It melts at 243° with decomposition and partially sublimes in transparent needles, the greater portion however, being decomposed. Its powder causes sneezing; it has a bitter taste and is quite odourless, but its solution imparts a very unpleasant and exceedingly persistent smell to the skin (Erdmann). Like isatin it gives a crystalline silver ammonium compound, which is of the colour of wine lees (*lie de vin*). It also forms compounds with the acid alkali sulphites. When a solution of chlorisatin is treated with caustic potash, it first becomes deep red and then pale yellow, while, when the solid compound is treated in the same way, it becomes almost black and gradually dissolves, more rapidly on heating, forming a light yellow solution. *Chorisatic acid*, $C_6H_3Cl(NH_2)CO.CO_2H$, is thus formed, but is very unstable and decomposes immediately into chlorisatin and water when liberated from its salts.

Potassium chlorisatate, $C_6H_3Cl(NH_2)CO.CO_2K$, crystallizes in light yellow needles or nacreous scales, is readily soluble in water, with difficulty in alcohol and has a very bitter taste. Other salts have been prepared from this by double decomposition, the following being characteristic.

Lead chlorisatate, $(C_6H_3Cl.NH_2.CO.CO_2)_2Pb+2H_2O$, forms a lustrous yellow, gelatinous precipitate, which soon becomes

[1] *Journ. Prakt. Chem.* [2] xxxiii. 49.

crystalline and assumes a splendid scarlet-red colour. It forms a yellow solution in boiling water and separates on cooling in scarlet granules.

The copper salt is a yellowish brown precipitate, which suddenly becomes deep blood-red coloured and is deposited as a heavy, granular powder. This remarkable property has been carefully investigated by Erdmann in the case of the corresponding salt of dichlorisatic acid, which behaves in a precisely similar manner.

Dichlorisatin, $C_8H_3Cl_2NO_2$, is formed, together with chlorisatin, by the action of chlorine on indigo suspended in water and is separated from the mono-substitution product by recrystallization from alcohol, in which it is much more readily soluble. It crystallizes in small, red plates, needles or four-sided prisms, melts at 186° (Dorsch), dissolves at 14° in 29·3° of alcohol, of sp. gr. 0·830, and combines with the acid alkali sulphites.

It forms a deep red solution in caustic potash, which becomes pale yellow on heating, *dichlorisatic acid*, $C_6H_2Cl_2(NH_2)CO.CO_2H$ being formed. This substance is precipitated by acids from the concentrated solution as a yellow powder, which is readily soluble in water and decomposes at 100° into water and dichlorisatin; this decomposition takes place in solution at 60°, the light yellow colour changing to reddish yellow and dichlorisatin being deposited on cooling.

Potassium dichlorisatate, $C_6H_2Cl_2(NH_2)CO.CO_2K + H_2O$, crystallizes from alcohol in light yellow plates or needles, which have a metallic lustre.

Its solution gives a yellow precipitate with lead acetate, which does not change its colour.

Copper dichlorisatate, $(C_6H_2Cl_2(NH_2)CO.CO_2)_2$ Cu, is obtained as a precipitate resembling ferrous hydroxide, which after a few seconds becomes flocculent and coloured pale greenish yellow and is finally deposited as a heavy, carmine-red, granular powder. A microscopic examination shows that hair-like or foliaceous groups of crystals are formed when the greenish colouration appears, and that when the colour changes to red, which appears first at isolated spots and is then rapidly transmitted through the entire mass, these crystals are replaced by irregular, transparent, red granules.

The dry, carmine-red powder which is well adapted for use as a pigment, takes a gold lustre when pressed with a hard body (Erdmann).

Bromisatin, $C_8H_4BrNO_2$, was obtained by Erdmann in small quantity, accompanied by a much larger amount of dibromisatin, by the action of bromine on indigo, while Laurent could only obtain the di-substitution product by the action of bromine on isatin. Hofmann, however, found that it is formed when isatin is treated with bromine water, even in the sunlight. It corresponds to chlorisatin in all its properties, and the similarity between these substances is so great that Hofmann referred to Erdmann's and Laurent's papers on chlorisatin for an account of its chemical behaviour.[1] It melts at 255° (Baeyer).

Bromisatic acid and its salts, which have been examined by Gericke, also resemble the corresponding chlorine compounds in every respect.[2]

Dibromisatin, $C_8H_3Br_2NO_2$, is best prepared, according to Baeyer, by treating a solution of isatin in glacial acetic acid, saturated at 100°, with about twice as much bromine as is necessary for the formation of dibromisatin and then heating for 15-20 hours on the water bath. It separates on cooling in orange-coloured needles, which are purified by conversion into potassium dibromisatate, which is only slightly soluble in water.[3]

Dibromisatin crystallizes from alcohol in four-sided prisms, which melt at 250°, and is much more readily soluble than the monobromo-compound. According to Baeyer, this is obviously due to the fact that the first bromine atom takes the para-position and the second the ortho-position to the nitrogen atom. The effect of the bromine atom in the ortho-position is also shown by the fact that the salts of dibromisatin and dibromisatic acid itself are much more stable than the derivatives of bromisatin. The second bromine atom, however, as will subsequently be shown, is actually situated in the meta-position.

Potassium dibromisatin, $C_8H_2KBr_2NO_2$, is obtained, according to Laurent, by the addition of alcoholic potash to a hot alcoholic solution of isatin, in the form of black spangles, which appear blue by transmitted light. It is also formed as a bluish violet powder by the action of dilute caustic potash solution on ethyl-dibromisatin (Baeyer).

Silver dibromisatin, $C_8H_2AgBr_2NO_2$, is prepared in a similar manner to silverisatin and is a brownish violet powder (Baeyer).

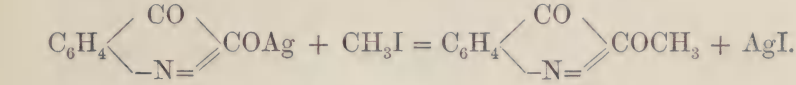
Dibromisatic acid, $C_6H_2Br_2(NH_2)CO.CO_2H$, is formed by the

[1] *Ann. Chem. Pharm.* liii. 40. [2] *Journ. Prakt. Chem.* xcv. 176.
[3] *Ber. Deutsch. Chem. Ges.* xv. 2098.

decomposition of its potassium salt and is a yellow powder, readily soluble in water, which is converted into dibromisatin by drying.

Potassium dibromisatate, $C_6H_2Br_2(NH_2)CO.CO_2K + H_2O$, is formed by heating dibromisatin with caustic potash and crystallizes in lustrous, straw-yellow needles, which are only slightly soluble in water. The copper salt behaves in a similar manner to that of dichlorisatic acid (Erdmann).

2315 *Ethers of isatin and the bromisatins* are obtained by the action of alcoholic iodides on the silver compounds :[1]



Methylisatin, $C_8H_4(CH_3)NO_2$, crystallizes from hot benzene in tolerably large, blood-red prisms, melting at 101°—102°, and is, like the salts of isatin, a very unstable substance, changing spontaneously after a short time, and frequently immediately after its preparation, into *methylisatoïd*, $C_{17}H_{12}N_2O_4$, a yellow powder, which crystallizes from alcohol in small yellow needles, melting with decomposition at 219°, and is converted into isatic acid by boiling with caustic soda.

Methylbromisatin, $C_8H_3Br(CH_3)NO_2$, forms blood-red needles, which melt at 147° and readily change into *methylbromisatoïd*, which melts at 230°—231°.

Ethylbromisatin, $C_8H_3Br(C_2H_5)NO_2$, crystallizes from hot benzene in long, blood-red, prismatic needles, melting at 107°—109°. On the addition of caustic potash solution to its alcoholic solution, it is first coloured reddish violet and then yellow, bromisatic acid being formed. When preserved for some time, it changes into *ethylbromisatoïd*, $C_{18}H_{12}Br_2N_2O_4$, which is more rapidly formed when the original ether is dissolved in acetic anhydride. In this case the isatoïd is deposited after two days in orange-yellow needles, which melt with decomposition at 244°—245° and dissolve in dilute, boiling caustic potash solution with a red colour, which soon changes to yellow, bromisatic acid being formed.

The constitution of these isatoïd ethers is quite unknown ; their empirical formulæ correspond to compounds of isatin or bromisatin with the ethers of these :

$$C_8H_5NO_2 + C_8H_4(CH_3)NO_2 = C_{17}H_{12}N_2O_4.$$
$$C_8H_4BrNO_2 + C_8H_3Br(C_2H_5)NO_2 = C_{18}H_{12}Br_2N_2O_4.$$

[1] Baeyer and Oekonomides, *ibid.* xvi. 2093.

Ethyldibromisatin, $C_8H_2Br_2(C_2H_5)NO_2$, crystallizes from alcohol in blood-red, spherical aggregates, containing alcohol of crystallization, which is soon lost in the air; the crystals become dull and then melt at 87°—89°. Dilute caustic potash converts it into potassium dibromisatin. It does not change into an isatoïd ether either spontaneously or on treatment with acetic anhydride.

Ethyl dibromisatate, $C_6H_2Br_2(NH_2)CO.CO_2.C_2H_5$, is formed by the action of ethyl iodide on silver dibromisatate and crystallizes in yellow tablets, which melt at 105° and are not converted into ethyl dibromisatin, but into dibromisatin on heating:

$$C_6H_2Br_2\begin{cases}NH_2\\CO.CO.OC_2H_5\end{cases} = C_6H_2Br_2\begin{cases}N\\CO\end{cases}\!\!>C.OH + HO.C_2H_5.$$

2316 *Nitro-isatin*, $C_8H_4(NO_2)NO_2$, is obtained by the addition of the calculated quantity of potassium nitrate to a solution of isatin in ten parts of sulphuric acid, which is cooled by a freezing mixture. After standing for some time, the liquid is poured on to ice and the separated product crystallized from alcohol. It forms yellow needles, which crystallize in rosette-shaped aggregates, melt at 226°—230° and form a reddish-yellow solution in caustic potash, which does not become lighter coloured on heating.[1]

Nitrobromisatin, $C_8H_3Br(NO_2)NO_2$, is prepared from bromisatin in a similar manner to nitro-isatin and crystallizes from alcohol in orange-yellow, warty masses, composed of small plates, which melt with decomposition at 237°. It forms a dark red solution in caustic soda, an orange-yellow precipitate being then produced, so that the colour of the solution becomes lighter. This precipitate dissolves when the solution is boiled and does not separate out again on cooling.[2]

Isatinsulphonic acid, $C_8H_4NO_2.SO_3H + 2H_2O$. When indigo is dissolved in fuming sulphuric acid, *indigo-blue sulphuric acid* or *indigotindisulphonic acid*, $C_{16}H_8N_2O_2(SO_3H)_2$, is formed, the sodium salt of which is brought into the market under the name of indigo-carmine. Gustav and Adolph Schlieper obtained isatinsulphonic acid, or as they named it *isatinsulphuric acid*, by the oxidation of this with hot, dilute sulphuric acid and potassium dichromate. They prepared the potassium salt by the addition of potassium nitrate to the hot, filtered solution, con-

[1] Baeyer, *Ber. Deutsch. Chem. Ges.* xii. 1312.
[2] Dorsch, *Journ. Prakt. Chem.* [2], xxxiii. 53.

verted this into the barium salt and finally liberated the free acid with sulphuric acid.[1] It forms a yellow, crystalline mass, which has a silky lustre and a strongly acid taste, dissolves readily in water, with more difficulty in alcohol, and becomes anhydrous at 100°. Nitric acid does not attack it, even on boiling, while potassium chlorate and hot hydrochloric acid convert it gradually into chloranil. Its solution dyes silk and wool orange-red.

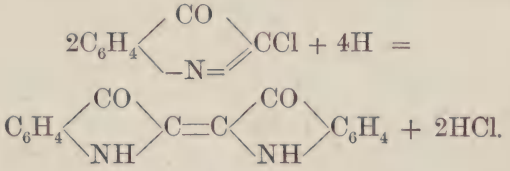
Potassium isatinsulphonate, $C_8H_4NO_2SO_3K + H_2O$, forms a crystalline powder, consisting of golden-yellow needles, which dissolve in about 20 parts of cold water, more readily in hot water, and are not attacked by boiling concentrated hydrochloric acid.

Sodium isatinsulphonate, $C_8H_4NO_2SO_3Na + 2H_2O$, is obtained by the addition of a large amount of common salt to the hot, saturated solution of the potassium salt. It crystallizes on cooling in large, bright red tablets.

Barium isatinsulphonate, $(C_8H_4NO_2SO_3)_2Ba + 4H_2O$, is formed when a barium salt is added to an isatinsulphonate in acid solution and even when the free acid is added to a solution of barium chloride or nitrate. It forms brilliantly lustrous, scarlet-red, crystalline scales, which are insoluble in alcohol and slightly soluble in cold, more readily in hot water.

Sulpho-isatic acid, $C_6H_3(NH_2)(SO_3H)CO.CO_2H$. The salts of this acid are formed when the preceding compounds are heated with alkalis. They are of a yellow colour, crystallize well, and are reconverted into isatinsulphonates by hydrochloric acid.

Isatin chloride, C_8H_4NOCl, is obtained by heating isatin with benzene and phosphorus chloride. It crystallizes on cooling in small, brown needles, forms blue solutions in ether, alcohol, &c., rapidly decomposes in moist air and is converted into isatin by caustic potash, while ammonium sulphide converts it into indigo-blue:[2]

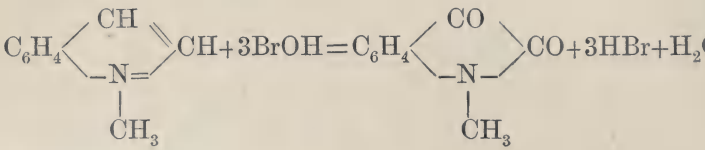


Bromisatin chloride, $C_8H_3BrNOCl$, is prepared in the same manner from bromisatin and crystallizes in small, reddish-brown

[1] *Ann. Chem. Pharm.* cxx. 1.
[2] Baeyer, *Ber. Deutsch. Chem. Ges.* xi. 1296; xii. 456.

lustrous needles, which form solutions of this colour in alcohol, ether and benzene and are converted into bromindigo by the action of hydriodic acid.[1]

2317 *Methylpseudo-isatin*, $C_8H_4O_2NCH_3$, is formed when methylindol, $C_8H_6NCH_3$, or methylindolcarboxylic acid, $C_8H_5(NCH_3)CO_2H$, is treated with solution of sodium hypobromite and the crystalline bromine compound, $C_8H_6Br_2NCH_3$, which is formed, decomposed with caustic soda solution. The formation of the methylpseudo-isatin can be simply explained by the following equation:



It can also be obtained by the use of sodium hypochlorite.[2] It crystallizes from hot water in splendid red needles, which melt at 134°, and in its other properties resembles the ethyl compound, which has been more carefully investigated.

Ethylpseudo-isatin, $C_8H_4O_2.NC_2H_5$, which is prepared in a similar manner from ethylindolcarboxylic acid, was first obtained by Baeyer by dissolving ethylpseudo-isatin-*α*-ethyloxime (p. 94) in acetic acid and treating it with zinc dust, the mixture being well cooled, until the yellow colour of the solution disappeared. It was then diluted with water and boiled with ferric chloride for five or ten minutes. The ethylpseudo-isatin was then extracted with ether, removed from the ethereal solution by caustic soda, liberated by acidification and again extracted with ether. It remained on evaporation in blood-red tablets, similar to those of azobenzene.[3]

It is readily soluble in alcohol and hot water, with greater difficulty in ether, melts at 95° and volatilizes when more strongly heated, with formation of a greenish-yellow vapour. It dissolves in alkalis to a yellow solution, a salt of *ethylisatic acid*, $C_6H_4[N(C_2H_5)H]CO.CO_2H$, being formed, whereas isatin itself is first converted into its violet salt and then into the yellow isatate. This salt yields ethylpseudo-isatin on decomposition by acids.

[1] *Ber. Deutsch. Chem. Ges.* xii. 1315.
[2] Fischer and Hess, *ibid.* xvii. 563.
[3] *Ibid.* xvi. 2193.

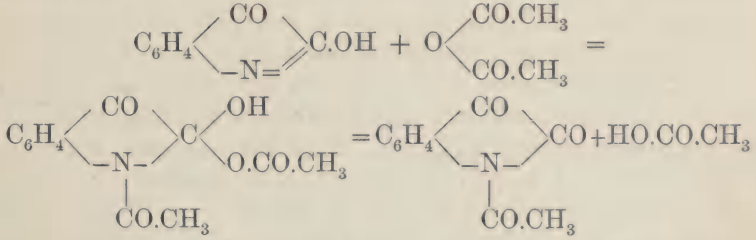
Barium ethylisatate, $(C_{10}H_{10}NO_3)_2Ba$, is formed by dissolving ethylpseudo-isatin in baryta water and crystallizes from the concentrated solution in pure yellow, lustrous needles. When silver nitrate is added to its solution, *silver ethylisatate* separates in flat, yellow needles, which are slightly soluble in water.

Ethylpseudo-isatin yields an indophenin with sulphuric acid and benzene containing thiophene, which forms a blue solution in ether and is thus distinguished from that given by isatin, which is absolutely insoluble in ether.

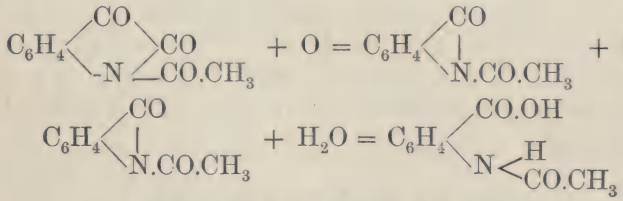
It is not attacked by concentrated hydrochloric acid even at 150° and therefore contains the ethyl group very firmly combined, while ethylisatin is saponified by dilute alkalis even in the cold (Baeyer).

Benzylpseudo-isatin, $C_8H_4O_2NCH_2.C_6H_5$, has been prepared by the oxidation of benzylindol (p. 39) and crystallizes from hot water in silky, red needles, melting at 131°.[1]

Acetylpseudo-isatin, $C_8H_4O_2NCO.CH_3$, is formed by heating isatin with acetic anhydride:



It crystallizes from benzene in yellow, prismatic needles, which are slightly soluble in cold water, readily in alcohol and melt at 141°. On boiling with water, or more rapidly with hydrochloric acid, it is converted into isatin, while chromic acid oxidizes it to acetorthamidobenzoic acid, the first product being probably acetanthranil (Part IV., p. 240), which then combines with water:[2]



[1] Antrick, *Ann. Chem. Pharm.* ccxxvii. 364.

[2] v. Meyer and Bellmann, *Journ. Prakt. Chem.* [2], xxxiii. 31.

Acetylisatic acid, $C_6H_4(NH.CO.CH_3)CO.CO_2H$, is obtained by the addition of dilute sulphuric acid to a solution of acetylpseudo-isatin in cold, dilute caustic soda, as a yellow crystalline powder, which crystallizes from alcohol in colourless needles, melting at 160°, and is converted into isatin by boiling hydrochloric acid.[1] Sodium amalgam reduces it in acetic acid solution to acetylhydridinic acid (p. 54).

Acetylisatic acid is more stable than isatic acid, while ethylisatic acid is not known in the free state. The stability of isatic acid is therefore increased when the hydrogen of the amido-group is replaced by an acid radical, but is diminished by the introduction of an ethyl group (Baeyer).

Acetylbromopseudo-isatin, $C_8H_3BrO_2NCO.CH_3$, is formed by boiling bromisatin with acetic anhydride for some time and crystallizes from benzene in straw-yellow prisms, melting at 170°—172°.

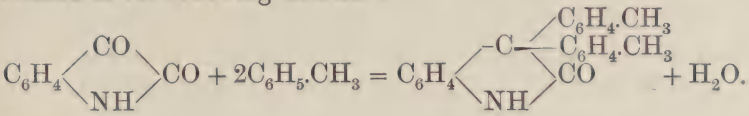
Acetylbromisatic acid, $C_6H_3(NH.CO.CH_3)CO.CO_2H$, is obtained by the addition of an acid to a solution of acetylbromopseudo-isatin; it separates out in fascicular groups of colourless needles, which melt at 178°—180° with evolution of gas. The acetyl group in this compound is more firmly combined than in acetylisatic acid, since it does not, like the latter, give the indophenin reaction with benzene and sulphuric acid in presence of thiophene.[2]

2318 *Tolu-isatin*, $C_{22}H_{19}NO$. Pure benzene does not react with isatin and sulphuric acid, whereas toluene immediately enters into combination when it is shaken up with a solution of isatin in sulphuric acid, the red colour changing to greenish-brown and toluisatin being formed. It crystallizes from alcohol in colourless, lustrous needles, which melt at 200°—201°, and are insoluble in caustic potash even on boiling, but dissolve in fused caustic potash without decomposition.

Ethyltolu-isatin, $C_{22}H_{18}(C_2H_5)NO$, is obtained by heating tolu-isatin with ethyl iodide and sodium ethylate and crystallizes from ether in small plates, which melt at 108° and are not attacked by boiling alcoholic potash or by heating with hydrochloric acid. The same compound is formed when ethylpseudo-isatin is shaken up with toluene and sulphuric acid, as well as when ethyltolindolcarboxylic acid is oxidized with sodium hypochlorite.[3]

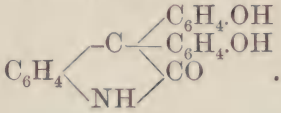
[1] Suida, *Ber. Deutsch. Chem. Ges.* xi. 584.
[2] Baeyer, *ibid.* xv. 2096.
[3] Hegel, *Ann. Chem. Pharm.* xxxii. 219.

Tolu-isatin is therefore a derivative of pseudo-isatin and is formed in the following manner:



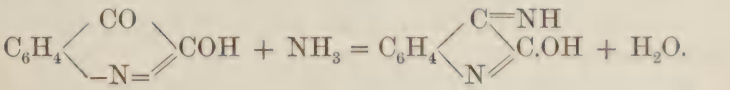
It may therefore be termed *ditolyloxindol*.[1]

Phenolisatin, $C_{20}H_{15}NO_3$, is formed when sulphuric acid is added to a solution of isatin in phenol and crystallizes from chloroform in fine, white needles, which melt at 220°, are readily soluble in alkalis and are reprecipitated by acids. It probably has the following constitution:



Isatin not only condenses with hydrocarbons and phenols, but also with tertiary bases (Baeyer and Lazarus).

2319 *Imesatin*, $C_8H_6N_2O$, is formed by the action of ammonia on isatin:



In order to obtain it, ammonia is passed into warm ether in which isatin is suspended. It crystallizes on evaporation in odourless, dark yellow, rectangular prisms and is converted into isatin by heating with alkalis or acids (Laurent).

Laurent obtained other complex substances by the action of ammonia on isatin in presence of alcohol.

Isatindiamide, $C_{16}H_{12}N_4O_2$, is the name given by Sommaruga to a substance, which is formed among others when isatin is heated to 100° with alcoholic ammonia. It crystallizes in light yellow, matted needles, which are insoluble in water and only dissolve slightly in alcohol.

Isatindiamide hydrochloride, $C_{16}H_{12}N_4O_2.HCl$, forms a yellow, crystalline powder, which is scarcely soluble in cold, only slightly in hot water and loses hydrochloric acid when boiled with water.

Isatindiamide sulphate, $C_{16}H_{12}N_4O_2.SO_4H_2$, crystallizes in light

[1] Baeyer and Lazarus, *Ber. Deutsch. Chem. Ges.* xviii. 2638.

yellow needles, which form groups resembling "crabs' eyes" (*lapis cancrorum*).

Monamido-isatin, $C_{16}H_{11}N_3O_3$, is formed by boiling the diamide with caustic potash and crystallizes from alcohol in small, yellowish needles, which are readily soluble in alkalis, with which they combine.

Oxydimidodiamido-isatin, $C_{16}H_{14}N_6O_3$, is obtained together with the diamide and crystallizes from hot water or alcohol in needles, which taste sweet and then acrid. It combines with acids to form salts, which are crystalline and yield solutions which exhibit a splendid, bluish-red fluorescence.[1]

Phenylhydrazine-imesatin is formed when an aqueous solution of isatin and phenylhydrazine hydrochloride is heated to boiling:

$$\begin{array}{l} N{=\!=}C.OH \\ | \qquad\quad | \\ C_6H_4{-}CO \end{array} + N_2H_3.C_6H_5 = \begin{array}{l} N{=\!=}C.OH \\ | \qquad\quad | \\ C_6H_4{-}C{=}N_2H.C_6H_5 \end{array} + H_2O.$$

It crystallizes from boiling alcohol in fine, yellowish-red needles, melting at 210°—211°. A solution of one part of isatin in 2,000 parts of water gives a precipitate of this compound after a few moments, and even when the solution is only one-tenth of this strength the fine needles can be detected.[2]

Phenylimesatin, $C_8H_5(C_6H_5)N_2O$, is prepared by heating aniline with isatin and a little absolute alcohol:[3]

$$C_6H_4\left\langle\begin{array}{l} CO \\ -N{=} \end{array}\right\rangle C.OH + NH_2.C_6H_5 = C_6H_4\left\langle\begin{array}{l} C{=}N.C_6H_5 \\ N \end{array}\right\rangle C.OH + H_2O.$$

It is also formed when aniline is heated with dichloracetic acid.[4]

Phenylimesatin crystallizes from alcohol in stellate groups of yellow, pointed prisms and is decomposed into isatin and aniline by heating with alkalis and hydrochloric acid.

If the homologues of aniline be employed in this reaction, homologous imesatins and isatins are formed, the best known of which is that prepared from paratoluidine, which will therefore

[1] Sommaruga, *Ann. Chem. Pharm.* cxc. 367; cxciv. 85; *Monatsh. Chem.* i. 575.

[2] E. Fischer, *Ber. Deutsch. Chem. Ges.* xvii. 577.

[3] Engelhardt, *Journ. Prakt. Chem.* [1], xix. 358.

[4] P. J. Meyer, *Ber. Deutsch. Chem. Ges.* xvi. 2942; see also the two following references.

be described here, although it belongs to the group of compounds with nine atoms of carbon.

Paratolylparamethylimesatin, $C_{16}H_{16}N_2O$, was prepared by P. J. Meyer by heating paratoluidine with dichloracetic acid.[1] Dibromacetic acid may also be employed in its preparation.

Paratolylparamethylamidoxindol, is the first product of the reaction:

$$2CH_3.C_6H_4.NH_2 + \begin{array}{l} CHCl_2 \\ | \\ CO{\cdot}OH \end{array} =$$

$$CH_3.C_6H_3\left\langle\begin{array}{l} CH{-}NH(C_6H_4.CH_3) \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \rangle CO \\ NH \end{array}\right. + 2HCl + H_2O.$$

This substance crystallizes from hot alcohol in small, white needles and forms a solution which has a persistent, biting taste, rapidly absorbs oxygen from the air and is oxidized by an ammoniacal silver solution, the imesatin being formed and a splendid silver-mirror deposited:[2]

$$CH_3.C_6H_3\left\langle\begin{array}{l} CH{-}NH(C_6H_4.CH_3) \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \rangle CO \\ NH \end{array}\right. + O =$$

$$CH_3.C_6H_3\left\langle\begin{array}{l} C{=}N.C_6H_4.CH_3 \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \rangle C.OH \\ N \end{array}\right. + H_2O.$$

It is insoluble in water and crystallizes from hot alcohol in golden-yellow, lustrous needles or plates, which melt at 259° to a dark red liquid. When treated with concentrated caustic soda solution, it forms a salt, which crystallizes in red prisms and is decomposed by water.

Ethyltolylparamethylimesatin, $C_{16}H_{15}(C_2H_5)N_2O$, is obtained by heating the imesatin with ethyl bromide and a solution of sodium ethylate. It crystallizes in large, orange-red prisms, which fuse at 151°—152° to a blood-red liquid.

Acetyltolylparamethylimesatin, $C_{16}H_{15}(C_2H_3O)N_2O$, is formed when the imesatin is heated with acetic anhydride and crystallizes from alcohol in small, deep red, lustrous needles, fusing at 121°—122° to a blood-red liquid, which solidifies to a vitreous mass.

Paramethylimesatin, $C_8H_4(CH_3)NO.NH$, is obtained by heating tolylmethylimesatin with alcoholic ammonia and crystallizes

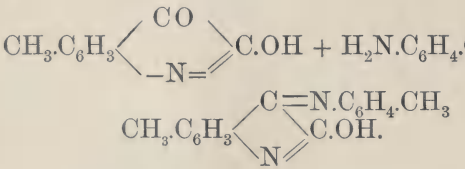
[1] *Ber. Deutsch. Chem. Ges.* xvi. 2261. [2] Duisberg, *ibid.* xviii. 190.

from a large amount of hot water in fine, soft needles, which dry to a silver-lustrous mass resembling paper. It shows no similarity to Laurent's imesatin and is probably homologous with isatin-diamide.

2320 *Paramethylisatin*, $C_8H_4(CH_3)NO_2$, is prepared by the action of hydrochloric acid on tolylmethylimesatin and separates from alcohol in large, deep red, transparent crystals, while it crystallizes from water in lustrous, red plates, melting at 187°. It dissolves in alkalis, forming a deep violet-coloured solution, which changes to yellow on standing or heating, a paramethyl-isatate being formed, which yields the original paramethylisatin on decomposition with acids.

This compound is homologous with isatin and metameric with its methyl ether.

On heating with alcohol and paratoluidine the original compound is again formed:



It is therefore a lactim, and not a lactam, as its formation from dichloracetic acid would seem to show. The fact that it forms alkali salts is also in favour of this conclusion.

Phenylparamethylimesatin, $C_9H_7(NC_6H_5)NO$, has been prepared from paramethylisatin and aniline, and crystallizes in thick, yellowish-red tablets or prisms, melting at 239°—240°.

Phenylhydrazineparamethylimesatin, $C_9H_7(N_2H.C_6H_5)NO$, crystallizes from hot alcohol in golden-yellow needles, which sublime at 240° and only melt at 300°, decomposition accompanied by evolution of gas taking place.[1]

Ethylparamethylpseudo-isatin or *Ethylpseudoparatolisatin*, $C_9H_6O_2(NC_2H_5)$, is formed by the action of cold, concentrated hydrochloric acid on ethyltolylparamethylimesatin, and also by the oxidation of ethylparatolindol with sodium hypochlorite.[2] It crystallizes from hot water or petroleum-spirit in blood-red needles or prisms, melting at 109°—110°, and forms a yellow solution in alkalis. It resembles ethylpseudo-isatin in its behaviour

[1] Panaotovic, *Journ. Prakt. Chem.* [2], xxxiii. 73.
[2] Hegel, *Ann. Chem. Pharm.* ccxxxii. 214.

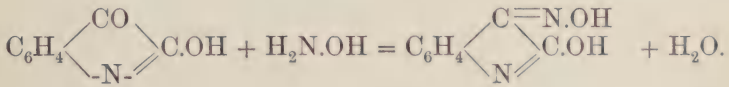
towards reducing agents, yielding a yellow substance, but no colouring-matter of the indigo group.

The following compounds have been prepared by Hegel from the corresponding indols:

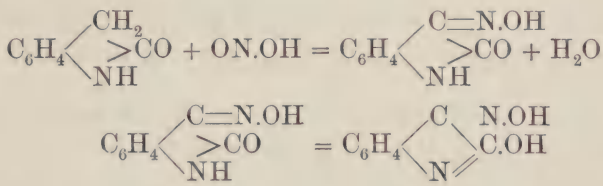
	Melting-point.
Methylpseudoparatolisatin, red needles . .	148°
Methylpseudorthotolisatin, brick-red needles	157°

Acetylparamethylpseudo-isatin, $C_9H_6O_2(NC_2H_3O)$, is obtained by the decomposition of acetyltolylmethylimesatin by means of hydrochloric acid, as well as by boiling paramethylisatin with acetic anhydride. It crystallizes from benzene in lemon-yellow needles, which melt at 172° and dissolve in caustic soda solution. On the addition of hydrochloric acid to this solution, *acetylparamethylisatic acid*, $C_6H_3(CH_3)(NH.CO.CH_3)CO.CO_2H$, is precipitated; it crystallizes from hot water in small, white needles, which melt with decomposition at 172° (Duisberg).

2321 *Isatinoxime* or *Isatoxime*, $C_8H_6N_2O_2$, was prepared by Baeyer and Knop, who named it *nitrosoxindol*[1] (p. 74), by passing nitrogen trioxide into a 1 per cent. aqueous solution of oxindol. It is also formed when hydroxylamine and isatin are brought together in solution in dilute alcohol:[2]



In its formation from oxindol, the first product is probably isonitroso-oxindol, which immediately undergoes intermolecular change similarly to pseudo-isatin:



Isatoxime crystallizes in very fine, long, golden-yellow needles, which are very slightly soluble in water, more readily in alcohol, and melt at about 202° with decomposition. It forms a dark reddish brown coloured solution in alkalis, from which it is reprecipitated by acids.

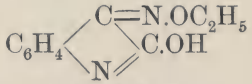
[1] *Ann. Chem. Pharm.* cxl. 34. [2] *Ber. Deutsch. Chem. Ges.* xvi. 517.

Silver isatoximate, $C_8H_5N_2O_2Ag$, is formed when ammonia is added to an alcoholic solution of silver nitrate and isatoxime, as an orange-coloured, gelatinous precipitate, which dries to a brick-red powder.

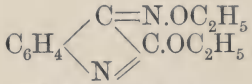
Ethyl isatoximate or *Isato-ethyloxime*, $C_8H_5N_2O_2(C_2H_5)$, is readily formed by the action of ethyl iodide on the silver salt, crystallizes from alcohol in fine, yellow needles, melting at 138°, and dissolves in caustic soda, forming a solution from which it is precipitated by carbon dioxide.

Silver ethyl isatoximate, $C_8H_4N_2O_2Ag(C_2H_5)$, is prepared in a similar manner to silver isatoximate, and is an amorphous brick-red powder.

Diethyl isatoximate or *Ethylisato-ethyloxime*, $C_8H_4N_2O_2(C_2H_5)_2$, is obtained when the preceding compound is allowed to stand for some time in contact with an ethereal solution of ethyl iodide. It remains after the evaporation of the ether as a light yellow oil, which solidifies at the ordinary winter temperature and rapidly changes to a viscid, yellowish-red mass. It dissolves with difficulty in cold caustic soda solution and is converted into isato-ethyloxime by it on boiling. Since the ethers of the oximes are stable substances, while those of isatin are very unstable, the constitution of these two ethyl ethers must be as follows:[1]

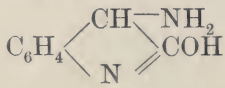


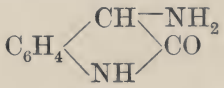
Isato-ethyloxime.



Ethylisato-ethyloxime.

2322 *Amidoxindol*, $C_8H_8N_2O$, is formed by the reduction of isatoxime with tin and hydrochloric acid. Its hydrochloride, $C_8H_8N_2O,HCl$, forms colourless warty masses and is decomposed by water with separation of a red resinous substance. It is quantitatively converted into isatin by the action of ferric chloride, cupric chloride or nitrous acid.[2] Its constitution is probably expressed by one of the following formulæ:





The ethers of isatoxime are also converted into isatin by reduction and subsequent oxidation.

[1] Baeyer and Comstock, *Ber. Deutsch. Chem. Ges.* xvi. 1704.
[2] Baeyer, *ibid.* xi. 1228.

Bromisatoxime, $C_8H_5BrN_2O_2$, is obtained by the addition of bromine water to a cold solution of isatoxime in the form of light yellow, lustrous needles, which are very slightly soluble in water, more readily in alcohol, and decompose at 240° without melting. It dissolves in caustic potash solution and is reprecipitated by acids (Baeyer and Knop).

Dibromisatoxime, $C_8H_4Br_2N_2O_2$, is formed by the combination of hydroxylamine with dibromisatin; it is slightly soluble in alcohol and crystallizes from glacial acetic acid in thick, light-yellow, pointed needles, which carbonize at about 255°.

Dibromisato-ethyloxime, $C_8H_3Br_2N_2O_2(C_2H_5)$, is prepared from the red silver salt of the preceding compound and ethyl iodide. It crystallizes from acetone in long, yellow, silky needles, melting at 115°—116°. It is converted into dibromisatin by successive reduction and oxidation (Baeyer and Comstock).

Tribromisatoxime, $C_8H_3Br_3N_2O_2$, is formed when an aqueous solution of isatoxime is heated with an excess of bromine. It is insoluble in water and crystallizes from boiling alcohol in dirty violet needles, which melt at 162° and commence to sublime in red prismatic needles at 190° (Baeyer and Knop).

Diazo-isatoxime chloride, $C_8H_5N_4O_2Cl$, is obtained by adding amyl nitrite to an alcoholic solution of paramido-oxindol (p. 22) acidified with hydrochloric acid:

$$2NO.OH + HCl + H_2N.C_6H_3\begin{cases}CH_2\\ \\ NH\end{cases}CO =$$

$$ClN{=}NC_6H_3\begin{cases}C{=}N.OH\\ >CO\\ NH\end{cases} + 3H_2O.$$

It separates in golden-yellow needles, which explode on heating, and is converted into isatoxime by boiling with alcoholic hydrochloric acid.[1]

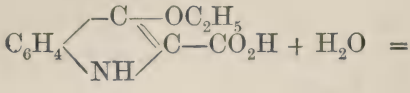
Paramethylisatoxime, $C_9H_8N_2O_2$, is formed by the action of hydroxylamine on paramethylisatin (p. 90) and crystallizes in long yellow prisms, melting at 225°—226°.[2]

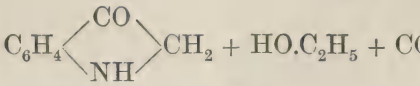
2323 *Pseudo-isatin-α-oxime*, $C_8H_6N_2O_2$, which was formerly known as *nitroso-indoxyl* (p. 40), is prepared by the action of nitrous acid on ethylindoxylic acid. This assumes the elements of water and is then converted with elimination of alcohol and

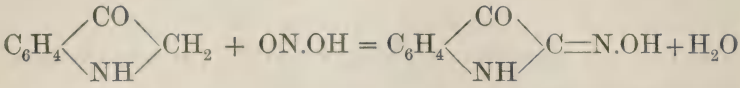
[1] Gabriel and Meyer, *Ber. Deutsch. Chem. Ges.* xiv. 832, and 2332; Gabriel, *ibid.* xvi. 517.

[2] P. J. Meyer, *ibid.* xvi. 2261.

carbon dioxide into pseudo-indoxyl, which is then acted upon by the nitrous acid (Baeyer):



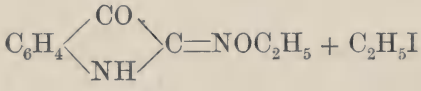


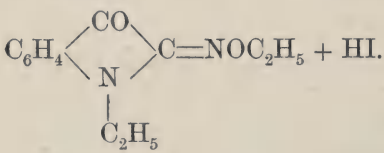


It crystallizes from alcohol in strongly lustrous, yellow or orange-coloured needles, which decompose at about 200° without melting at any definite temperature. It is converted into isatin by reduction and subsequent oxidation, while ammonium sulphide reduces it to indigo-blue.

Pseudo-isatin-α-ethyloxime, $C_8H_5N_2O_2(C_2H_5)$, is formed when the preceding compound is treated with sodium ethylate and ethyl iodide. It crystallizes in brownish-yellow plates, melting at 135°, dissolves in alcoholic potash with a violet and in alcoholic sodium ethylate with a blue colour. It can be converted into isatin and indigo-blue in the same way as pseudo-isatin-*α*-oxime.[1]

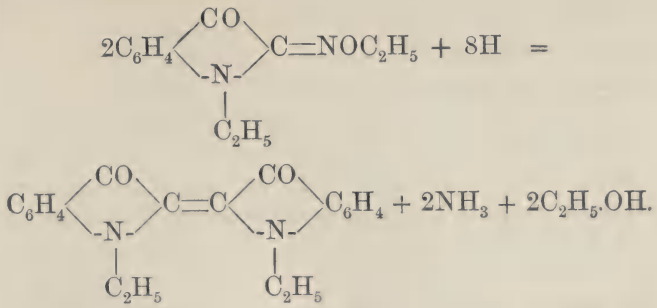
Ethylpseudo-isatin-α-ethyloxime, $C_8H_4N_2O_2(C_2H_5)_2$, is obtained by the further action of sodium ethylate and ethyl iodide on the preceding compound:



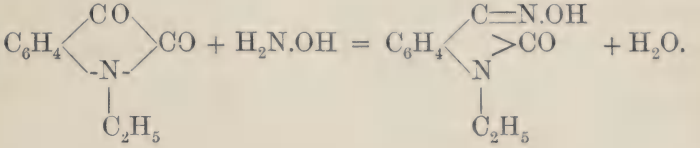


It crystallizes from hot water in yellow needles, which melt at 99° and sublime at a higher temperature. It is converted into *diethylindigo* by the action of ammonium sulphide:[2]

[1] Baeyer, *Ber. Deutsch. Chem. Ges.* xv. 782; xvi. 2191.
[2] *Ibid.* xvi. 2201.



Ethylpseudo-isatin-β-oxime, $C_8H_7O_2.N_2C_2H_5$, is the product of the combination of ethylpseudo-isatin with hydroxylamine:



It crystallizes from alcohol in yellow, four-sided prisms, melting at 160°—162°, does not yield an indigo colour when treated with ammonium sulphide and is converted into ethylpseudo-isatin by reduction followed by oxidation.[1]

2324 *Isatyde*, $C_{16}H_{12}N_2O_4$, was prepared by Erdmann by dissolving isatin in warm ammonium sulphide,[2] while Laurent obtained it by the action of the same reagent on an alcoholic solution of isatin.[3] He subsequently found that it is also formed when isatin is gently warmed with zinc and very dilute sulphuric acid.[4] The yellowish-red solution of isatin in glacial acetic acid is decolourized by zinc dust in the cold, but becomes coloured again on exposure to the air, while dioxindol is formed when its aqueous solution is boiled with zinc dust and a little hydrochloric acid, isatyde being however produced if the solution contain isatin in suspension (Baeyer). The latter substance is best prepared by boiling isatin with glacial acetic acid and zinc dust.[5] It is also formed when an aqueous solution of dioxindol is exposed to the air (Baeyer and Knop). It is a white, yellowish or reddish powder, which is almost insoluble in water and only

[1] *Ber. Deutsch. Chem. Ges.* xvi. 2196.
[2] *Journ. Prakt. Chem.* xxiv. 15.
[3] *Ibid.* xxv. 436; *Ann. Chim. Phys.* [3], iii. 382.
[4] *Ann. Chem. Pharm.* lxxii. 285.
[5] *Ber. Deutsch. Chem. Ges.* xii. 1309.

slightly soluble in alcohol, from which it crystallizes in oblique microscopic prisms.

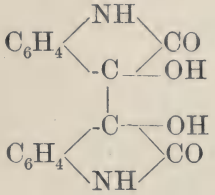
The substitution products of isatyde are formed by the reduction of the corresponding derivatives of isatin with ammonium sulphide.

Dithio-isatyde, $C_{16}H_{12}N_2O_2S_2$, termed *sulphisatin* by Erdmann and *sulphisathyde* by Laurent, is formed when sulphuretted hydrogen is passed into a boiling alcoholic solution of isatin, and forms a yellowish-grey powder, which is insoluble in water, but readily soluble in alcohol.

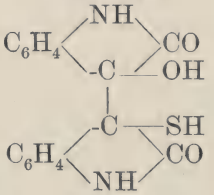
Thio-isatyde, $C_{16}H_{12}N_2O_3S$, was prepared by Laurent, who named it *sulphasathyde*, by gradually adding caustic potash to an alcoholic solution of dithio-isatyde. It is a colourless crystalline powder, which is insoluble in water and only slightly soluble in alcohol.

Isatyde may be considered from its method of formation to be the pinacone of isatin or more probably of pseudo-isatin, and the constitution of the preceding compounds can then be expressed by the following formulæ:

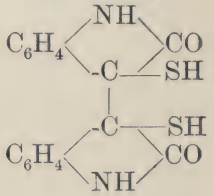
Isatyde.



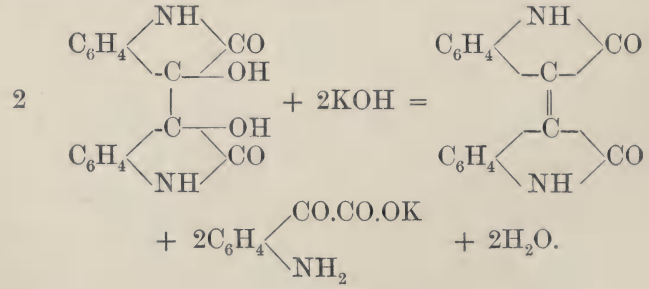
Thio-isatyde.



Dithio-isatyde.



Indin, $C_{16}H_{10}N_2O_2$, is formed when the compounds just described are boiled with alcoholic potash, isatic acid being also obtained when isatyde is employed. A simultaneous reduction and oxidation therefore take place:

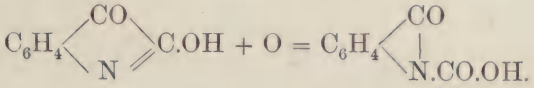


Indin is isomeric with indigo-blue and forms dark rose-coloured, microscopic crystals, which are insoluble in water and

only slightly soluble in alcohol. Knop obtained an isomeric, or possibly identical substance, as a violet-red amorphous powder by heating dioxindol with glycerol. When indin is treated with concentrated alcoholic potash, it yields the potassium salt of *indic acid*, $C_{16}H_{11}N_2O_3K$, which forms small black crystals, which are decomposed by water with formation of the original indin (Laurent).

Laurent and Knop have prepared other reduction products of isatin in addition to those already described, and Schützenberger has also obtained compounds of complex composition by heating isatin with hydriodic acid.[1]

2325. *Isatoic acid*, $C_8H_5NO_3$, was first prepared by Kolbe by the oxidation of isatin with a solution of chromium trioxide in glacial acetic acid. He found that it crystallizes from acetone in hard, yellow prisms, is decomposed into orthamidobenzoic acid and carbon dioxide when boiled with water or heated with bases or acids, and determined other of its properties. This was his last research [2] and was continued by E. v. Meyer and his pupils. This chemist noticed the great similarity existing between this acid and anthranilcarboxylic acid (Part IV. p. 240), from which it differs in its yellow colour and greater instability.[3] These differences were afterwards shown to be due to an admixed substance, which can be removed by means of nitrous acids or other oxidizing agents, the purified compound being identical with anthranilcarboxylic acid.[4] It is formed from isatin according to the following equation:



It is obtained from anthranil, as already mentioned, by heating with ethyl chlorocarbonic acid to 120°—140°.[5] It crystallizes from hot water in white needles, or when impure in yellow prisms, which melt at 230° and decompose into anthranil and carbon dioxide, while it changes into anthranilic acid when dissolved in alkalis or heated with strong hydrochloric acid.

Substitution products of isatoic acid. One atom of hydrogen in this acid can be replaced by the action of chlorine or bromine,

[1] *Bull. Soc. Chim.* 1865, 170.
[2] *Journ. Prakt. Chem.* [2], xxx, 467.
[3] *Ibid.* [2], xxx. 454.
[4] Meyer and Bellmann, *ibid.* [2], xxxiii. 18.
[5] Friedländer and Wleügel, *Ber. Deutsch. Chem. Ges.* xvi. 2227.

while derivations of anthranilic acid are formed on further treatment. The substituted isatoic acids can however be easily obtained by the oxidation of the corresponding isatin derivatives with a solution of chromium trioxide in glacial acetic acid; they form sandy, crystalline powders and can be crystallized from a mixture of alcohol and acetone [1]

Chlorisatoic acid, $C_8H_4ClNO_3$, forms long, rectangular, nacreous plates, which fuse at 265°—268° with decomposition accompanied by frothing. On boiling with hydrochloric acids it yields a chlororthamidobenzoic acid, which crystallizes from alcohol in long needles, melting at 204°. The chlorine atom in this compound must be in the para-position to the amido-group, since chlorisatin yields parachloraniline on heating with caustic potash. This constitution however has been ascribed to β-chlororthamidobenzoic acid, melting at 148° (Pt. IV. p. 25), which is converted by the diazo-reaction into the chlorosalicylic acid, which is prepared from parachlorophenol and tetrachloromethane. The question as to the actual constitutions of these bodies is therefore still an open one.

Dichlorisatoic acid, $C_8H_3Cl_2NO_3$, crystallizes in yellow prisms, apparently belonging to the rhombic system, which melt with decomposition at 254°—256°. It is only converted into dichloro-orthamidobenzoic acid by long continued boiling with concentrated hydrochloric acid; this substance melts at 222°—224°, and crystallizes in small needles.

Bromisatoic acid, $C_8H_4BrNO_3$, crystallizes in white, nacreous plates, which melt with decomposition at 270°—275°, and are converted into β-bromamidobenzoic acid by boiling with hydrochloric acid.

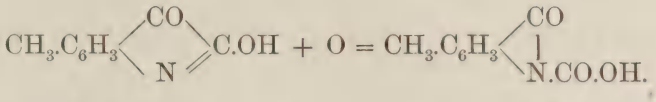
Dibromisatoic acid, $C_8H_3Br_2NO_3$, forms flesh-coloured groups of prisms, melting at 255°, and is converted into parametadibromo-orthamidobenzoic acid by continued boiling with hydrochloric acid. In the bromination of isatin, therefore, the second bromine atom takes the meta-position to the nitrogen atom and not the ortho-position, as stated by Baeyer (p. 80).

Nitro-isatoic acid, $C_8H_4(NO_2)NO_3$, is readily formed by the action of concentrated nitric acid on isatoic acid, and crystallizes from a mixture of acetone and alcohol in colourless, nacreous plates, which melt with decomposition between 220°—230°. On evaporation with hydrochloric acid, ε-nitro-amidobenzoic acid is formed, while it is reduced by tin and hydrochloric acid to α-diamidobenzoic acid (Pt. IV. p. 258).[2] The nitroxyl group is

[1] Dorsch, *Journ. Prakt. Chem.* [2], xxxiii. 32. [2] Kolbe, *ibid.* [2], xxx. 477.

therefore situated in the para-position with respect to the nitrogen atom.

Paramethylisatoic acid, $C_9H_7NO_3$, is formed by the oxidation of paramethylisatin with chromic acid:

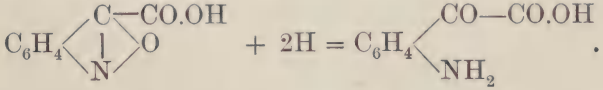


It is slightly soluble in water, more readily in boiling alcohol, ether and benzene, and very readily in acetone, from which it crystallizes in small, rhombic prisms. It decomposes suddenly at 245°, with formation of a voluminous mass, which melts above 300° with evolution of carbon dioxide. It is not decomposed by boiling water or dilute acids, but on heating with concentrated hydrochloric acid, it is resolved into carbon dioxide and *a*-amidometatoluic acid, which is converted into parahomosalicylic acid by the diazo-reaction.

Nitroparamethylisatoic acid, $C_9H_6(NO_2)NO_3$, crystallizes from benzene in light yellow, rhombic tablets, melting at 175°, and is converted into diamidotoluic acid by reduction.[1]

Anthroxanaldehyde, $C_8H_5NO_2$, is isomeric with isatin and is formed, together with anthranil, when orthonitrophenylhydroxyacrylic acid, $C_6H_4(NO_2)C_2H(OH)CO_2H$, is distilled with steam. It crystallizes from hot water or petroleum-spirit in long yellowish needles, melting at 72·5°, has a penetrating aromatic odour and yields a vapour which causes violent sneezing. Its solution in very dilute aqueous ammonia becomes coloured an intense violet-red when gently warmed with zinc dust. It dissolves readily in a concentrated solution of acid sodium sulphite, and, like other aldehydes, restores the colour to a solution of fuchsin which has been decolourized by sulphurous acid.

Anthroxanic acid, $C_8H_5NO_3$, which is metameric with isatoic acid, is formed by the oxidation of its aldehyde with alkaline permanganate. It is scarcely soluble in cold, but more readily in hot water, from which it crystallizes in fine white needles, melting at 190°—191°. It is converted into isatic acid by reduction with ferrous sulphate in ammoniacal solution:[2]



[1] Panaotovii, *Journ. Prakt. Chem.* [2], xxxiii. 57.
[2] Schillinger and Wleügel, *Ber. Deutsch. Chem. Ges.* xvi. 2222.

ETHENYLBENZENE OR PHENYLACETYLENE.

2326 Glaser first prepared this hydrocarbon from phenylpropiolic acid, $C_6H_5.C \equiv C.CO_2H$, by heating it with water to 120°, or submitting its barium salt to dry distillation. He then found that it is also formed when β-phenylbromethylene, $C_6H_5.CBr{=}CH_2$, is heated with alcoholic potash to 120°,[1] and Friedel prepared it in a similar manner from β-phenylchlorethylene.[2] According to Morgan, a much better yield is obtained when the latter compound, or the product of the action of phosphorus pentachloride on acetophenone, is passed over soda-lime heated to incipient redness.[3]

Phenylacetylene is a liquid, which has a characteristic, pleasant odour, boils at 139°—140° and combines with water to form acetophenone, $C_6H_5.CO.CH_3$, when it is shaken up with tolerably dilute sulphuric acid.[4] It forms metallic compounds, which correspond to those of acetylene (Glaser).

Sodium phenylacetylene, $C_6H_5.C_2Na$, is formed by the action of sodium on an ethereal solution of the hydrocarbon and is a white powder, which ignites in the air and combines directly with carbon dioxide to form sodium phenylpropiolate.

Silver phenylacetylene, $C_6H_5.C_2Ag + Ag_2O$, is obtained as a gelatinous precipitate when an alcoholic solution of the hydrocarbon is treated with ammoniacal silver solution. After drying it forms a light grey powder, which detonates on heating.

Cuprous phenylacetylene, $(C_6H_5.C_2)_2Cu_2$, is prepared in a similar manner, an ammoniacal cuprous chloride solution being employed, and is a light yellow precipitate, which, on agitation with alcoholic ammonia in presence of air, is converted into *diphenyldiacetylene*, $C_6H_5.C \equiv C - C \equiv C_6H_5$, which is the mother-substance of indigo and will be subsequently described.

Orthonitrophenylacetylene, $C_6H_4(NO_2)C_2H$, is formed when orthonitropropiolic acid is heated with water, and crystallizes from dilute alcohol in needles, melting at 81°—82°, has a pungent odour and gives a yellowish white silver compound

[1] *Ann. Chem. Pharm.* cliv. 151.
[2] *Compt. Rend.* lxvii. 1192.
[3] *Journ. Chem. Soc.* 1876, i. 164.
[4] Friedel and Balsohn, *Bull. Soc. Chim.* xxxv. 55.

and a red copper compound.[1] On treatment with zinc dust and ammonia, *orthamidophenylacetylene*, $C_6H_4(NH_2)C_2H$, is formed as a thick, yellow, oily liquid, which has a characteristic odour similar to that of naphthalene; in the dilute state however its vapour has a smell resembling that of an indigo-vat,[2] or, according to Müller, that of jasmine.

Paranitrophenylacetylene is obtained by heating paranitrophenylpropiolic acid with water, crystallizes in long needles, melting at 152°, and has an odour resembling that of cinnamon, while that of its ethereal solution is unpleasant and pungent. It forms a yellow silver compound and a red copper compound.[3]

[1] Baeyer, *Ber. Deutsch. Chem. Ges.* xiii. 2259.
[2] Baeyer and Landsberg, *ibid.* xv. 60.
[3] Müller, *Ann. Chem. Pharm.* ccxii. 133 and 139; Drewsen, *ibid.* ccxii. 158.

CUMENE GROUP.

2327 In the year 1838 Pelletier and Walter examined the oil, which is obtained as a by-product in the manufacture of illuminating gas from pine resin, and found in it both retin-naphtha (toluene) and a substance boiling at 150°, which they named *retinnyl*,[1] C_9H_{12}. In the same year Robert Kane obtained an isomeride of this, *mesitylene*, by the distillation of acetone, and gave to it the formula C_3H_4, since he believed that it bore the same relation to acetone, C_3H_6O, which he termed *mesitic alcohol*, as ethylene to ethyl alcohol.[2] Cahours and Gerhardt soon afterwards discovered that *cumol*, C_9H_{12}, a liquid boiling at 144°, is formed by the distillation of cuminic acid with baryta, and that the compound of this with sulphuric acid yields a barium salt differing from the corresponding retinnyl derivative.[3] About the same time they discovered in Roman cumin oil a compound, *cymol*, $C_{10}H_{14}$, which boils at 175°. Mansfield, as already mentioned (Pt. IV. p. 386), believed that he had also detected those two hydrocarbons in coal tar.

A more complete investigation of mesitylene, which was conducted by Hofmann, proved that it also has the molecular formula C_9H_{12}, but is quite distinct from the cumol prepared from cumic acid.[4] Cahours, who ascertained the presence of the latter hydrocarbon and its homologues in crude wood-spirit, made

[1] *Ann. Chim. Phys.* lxvii. 285 ; *Pogg. Ann.* xliv. 81.

[2] *Ibid.* xliv. 473. Reichenbach gave to acetone, or spirit of vinegar, which he found among the distillation products of wood, the name of *mesit* (μεσίτης, the mediator) : " Spirit of vinegar may be regarded as standing, to a certain extent, between alcohol and ether ; according to my observations it especially occupies the position of a mediator among the empyreumatic substances, since it unites many of these, which are either insoluble or only slightly soluble in one another, into a common whole, like tar or wood-vinegar " (Schweigg, *Journ. Chem. Phys.* lxix. 175.

[3] *Ann. Chem. Pharm.* xxxviii. 95.

[4] *Ibid.* lxxi. 121 ; Cahours, *ibid.* lxxiv. 106.

the important observation that the fraction boiling at 164°—168° has also the same composition and vapour density as cumol and mesitylene, but differs from both of these in its properties.[1]

In a short communication on the hydrocarbons of the benzene series, Warren de la Rue and Müller stated that the coal tar naphtha employed by them consisted chiefly of toluol, xylol and *pseudocumol*,[2] while Fritzsche found that the cumol extracted from tar yields a sulphuric acid derivative, the barium salt of which seems to agree in its properties with that of retinnylsulphuric acid.[3]

As it was then found that the fraction of coal-tar which boils at about 140° is not cumol but xylol, it appeared very probable that Mansfield's cymol would prove to be the next higher homologue of this, and therefore isomeric with the cumol from cumic acid, and this was soon experimentally established, the substance being therefore named *isocumol*,[4] *cumol from coal tar*,[5] or *pseudocumol*.[6]

It was afterwards proved by a more complete investigation that it is a mixture of mesitylene with another trimethylbenzene, for which the name of pseudocumol was retained,[7] and Jacobsen subsequently showed that the third trimethylbenzene is also present.[8]

The following hydrocarbons of the formula C_9H_{12} are now known:

s-Trimethylbenzene or Mesitylene
a-Trimethylbenzene or Pseudocumene } $C_6H_3(CH_3)_3$
v-Trimethylbenzene or Hemellithene

Paramethylethylbenzene
Metamethylethylbenzene } C_6H_4 (CH_3, C_2H_5)
Orthomethylethylbenzene

Isopropylbenzene or Cumene, $C_6H_5.CH(CH_3)_2$

Propylbenzene, $C_6H_5.C_3H_7$.

[1] *Ann. Chem. Pharm.* lxxvi. 286.
[2] *Ibid.* cxx. 339.
[3] *Jahresb. Chem.* 1862, 420.
[4] C. M. Warren, *Jahresber. Chem.* 1865, 514.
[5] Beilstein and Kögler, *Ann. Chem. Pharm.* cxxxvii. 317.
[6] Fittig, *ibid.* cxlv. 138.
[7] Fittig and Wackenroder, *ibid.* cli. 292.
[8] *Ber. Deutsch. Chem. Ges.* xix. 2511.

THE TRIMETHYLBENZENES $C_6H_3(CH_3)_3$

2328 *s-Trimethylbenzene or Mesitylene* is formed by heating acetone, C_3H_6O, mesitoxide, $C_6H_{10}O$, or phoron,[1] $C_9H_{14}O$ (Pt. I. p. 573), with sulphuric acid, as well as when allylene is dissolved in sulphuric acid and the allylenesulphonic acid which is formed distilled with water :[2]

$$3CH_3.C_2SO_3H + 3H_2O = (CH_3)_3C_6H_3 + 3SO_4H_2.$$

When methyl chloride is allowed to act upon metaxylene in presence of aluminium chloride, mesitylene is formed together with about four times the quantity of pseudocumene.

In order to prepare mesitylene, one volume of commercial acetone is mixed with dry sand in a large tubulated retort, a cold mixture of one volume of sulphuric acid and half a volume of water being then allowed to flow into the retort in a slow unbroken stream. The liquid is allowed to stand for twenty-four hours and then distilled; the first distillate consists of acetone and water, but is followed by the crude mesitylene, the receiver being changed as soon as oily bands appear in the retort. The distillate is washed with water and caustic soda, dried and purified by fractional distillation.[3]

Mesitylene is a strongly refractive liquid, which has a characteristic, not unpleasant odour, and boils at 163°.[4] It is oxidized by dilute nitric acid to mesitylenic acid, $C_6H_3(CH_3)_2CO_2H$, and uvitic acid, $C_6H_3(CH_3)(CO_2H)_2$, while chromic acid solution converts it into trimesic acid, $C_6H_3(CO_2H)_3$.

When picric acid is dissolved in hot mesitylene, the compound $C_9H_{12} + C_6H_3(NO_2)_3O$ separates on cooling in yellow plates.[5]

Hexhydromesitylene, $C_6H_9(CH_3)_3$, is obtained by heating mesitylene to 280° with phosphonium iodide. It is a liquid, which boils at 135°—138° and is not attacked by fuming nitric acid in the cold, but is converted into trinitromesitylene on warming.[6]

[1] Claisen, *Ber. Deutsch. Chem. Ges.* vii. 1168 ; Jacobsen, *ibid.* x. 885.
[2] Fittig and Schrohe, *ibid.* viii. 17.
[3] Fittig and Brückner, *Ann. Chem. Pharm.* cxlvii. 42.
[4] Fittig, *ibid.* cxli. 132.
[5] Robinet, *Compt. Rend.* xcvi. 500.
[6] Baeyer, *Ann. Chem. Pharm.* clv. 273.

α-Trimethylbenzene or *Pseudocumene* was first synthetically prepared by Ernst and Fittig, who brominated coal-tar xylene and treated the product with methyl iodide and sodium.[1] It may be obtained in this way both from bromoparaxylene[2] and from bromometaxylene,[3] as well as from the dibromotoluene, which is formed by the direct bromination of toluene.[4]

It is also a product of the action of aluminium chloride and methyl chloride on paraxylene and orthoxylene, while metaxylene yields mesitylene in addition.[5] Jacobsen has shown that the cumene, which is formed when phoron, $C_9H_{14}O$, is heated with zinc chloride or phosphorus pentoxide, is identical with pseudocumene, while mesitylene is obtained when sulphuric acid is employed.[6]

In order to separate it from coal-tar naphtha, the fraction which boils at 160°—168° is heated to 80°—90° with an equal volume of sulphuric acid, the mixture being well-agitated. Jacobsen found as the result of one experiment[7] that 390 ccm. are thus dissolved out of a total volume of 540 ccm. of the mixed hydrocarbons. The solution in sulphuric acid is then diluted with 180 ccm. of water, the liquid being well cooled; after about twenty-four hours, the lower layer, which consists almost entirely of dilute sulphuric acid, is removed and an additional quantity of 120 ccm. of water added to the residue. The liquid is then heated until the crystalline crust which has formed is redissolved and is then allowed to stand. The pseudocumenesulphonic acid separates out after some time, and a further quantity can be obtained by the concentration of the mother-liquor; thus, in the experiment mentioned above, 194 grms. were deposited during two days, while a second crop consisted of 18 grs. This product is then purified by recrystallization from dilute sulphuric acid. Mesitylenesulphonic acid and a little pseudocumenesulphonic acid remain in the mother-liquor. The pure hydrocarbon is liberated by heating the purified sulphonic acid to 173°—175° with hydrochloric acid or submitting it to dry distillation. The mixed sulphonic acids, from which the sulphuric acid has been removed by the addition of water in the way described, may also be heated to 100° with

[1] Baeyer, *Ann. Chem. Pharm.* cxxxix. 148.
[2] Fittig and Jannasch, *ibid.* cli. 283.
[3] Fittig and Laubinger, *ibid.* cli. 257.
[4] Jannasch, *ibid.* clxxvi. 286.
[5] Jacobsen. *Ber. Deutsch. Chem. Ges.* xiv. 2628.
[6] *Ibid.* x. 855. [7] *Ann. Chem. Pharm.* clxxxiv. 199.

hydrochloric acid, the mesitylene derivative alone being decomposed at this temperature.[1]

Pseudocumene has also been found in rock-oil from Burmah, and occurs, together with mesitylene, in all rock-oils which have hitherto been examined; American illuminating oil contains about 0·2 per cent. of this trimethylbenzene.[2] Pseudocumene boils at 169·5°;[3] it is oxidized by dilute nitric acid to xylic acid, paraxylic acid, $C_6H_3(CH_3)_2CO_2H$, and xylidic acid, $C_6H_3(CH_3)(CO_2H)_2$.

v-Trimethylbenzene or *Hemellithene* was prepared by Jacobsen by the distillation of *a*-isodurylic acid, $C_6H_2(CH_3)_3CO_2H$, with lime,[4] and was also detected by him in coal-tar. In order to prepare it, the fraction, which boils between 172°—180°, after repeated distillation is dissolved in warm sulphuric acid and the solution diluted until the mixed sulphonic acids crystallize out. They are then converted into the barium salts, from which the sodium salts, and finally the sulphamides, are prepared and readily obtained in the pure condition, pseudocumenesulphamide melting at 181°, and the corresponding hemellithene derivative at 195°.[5] The separation may be still more easily effected by converting the more difficultly soluble portion of the barium salt into the sodium salt and fractionally precipitating this with barium chloride until a sulphamide melting below 195° can no longer be prepared from the precipitate; the solution then contains the sodium sulphonate of hemellithene alone, and this is finally decomposed by heating with hydrochloric acid.[6]

It is a liquid boiling at 175°—175·5°, which does not solidify at −20° and is oxidized by dilute nitric acid to hemellithic acid, $C_6H_3(CH_3)_2CO_2H$.

Hexhydrocumene, C_9H_{18}, is the name given by Renard to a hydrocarbon which occurs with other similar compounds (Pt. IV. p. 6) in resin-spirit and boils at 147°—150°.[7] It is probably an addition-product of pseudocumene or hemellithene.

[1] Armstrong, *Ber. Deutsch. Chem. Ges.* xi. 1967.
[2] Engler, *ibid.* xviii. 2234; see also Markownikow, *Ann. Chem. Pharm.* ccxxxiv. 89.
[3] Jacobsen, *ibid.* xix. 2513.
[4] *Ibid.* xv. 1857.
[5] *Ber. Deutsch. Chem. Ges.* xix. 2511.
[6] *Ibid.* xix. 2520.
[7] *Ann. Chim. Phys.* [6], i. 229.

HALOGEN SUBSTITUTION PRODUCTS OF THE TRIMETHYLBENZENES.

2329 Dry chlorine acts very energetically upon cooled mesitylene, a mixture of mono-, di- and trichloromesitylene being formed. When the product is washed with caustic soda and dissolved in boiling alcohol, almost the whole of the trichloromesitylene separates on cooling. The greater portion of the alcohol is then removed from the filtrate by distillation and the residue precipitated with water, the compounds deposited being separated by fractional distillation.[1]

Monochloromesitylene, $C_6H_2Cl(CH_3)_3$, is a colourless liquid, which boils at 204°—206° and does not solidify at − 20°. Boiling chromic acid solution oxidizes it gradually to acetic acid, while dilute nitric acid converts it into chloromesitylenic acid, $C_6H_2Cl(CH_3)_2CO_2H$.

Dichloromesitylene, $C_6HCl_2(CH_3)_3$, crystallizes from alcohol in splendid, lustrous prisms, melting at 59°. It boils at 243°—244°, but readily volatilizes at the ordinary temperature. It is scarcely attacked by a boiling solution of chromic acid.

Trichloromesitylene, $C_6Cl_3(CH_3)_3$, was prepared by Kane, who named it *pteleyl chloride*, C_3H_5Cl, because he believed that the radical of this substance was also contained in ulmic acid (*ulmus*, πτελέα), a decomposition product of woody fibre.

It is also obtained, together with hexmethylbenzene, by the action of methyl chloride on a mixture of aluminium chloride and orthodichlorobenzene. In order to explain this remarkable formation, it may be assumed that the following reaction among others takes place:

$$C_6H_4Cl_2 + Al_2Cl_6 = C_6H_4ClAl_2Cl_5 + Cl_2.$$

The monochloromesitylene which is first formed is then further chlorinated.[2]

Trichloromesitylene crystallizes from boiling alcohol in fine needles, melts at 204°—205°, boils at 280° and readily sublimes in lustrous needles. It is scarcely attacked by boiling nitric acid, chromic acid or alkaline permanganate.

[1] Fittig and Hoogewerff, *Ann. Chem. Pharm.* cl. 323.
[2] Friedel and Crafts, *Ann. Chim. Phys.* [6], x. 411.

Monobromomesitylene, $C_6H_2Br(CH_3)_3$, is formed by the action of bromine on well-cooled mesitylene.[1] According to Schramm, it is best prepared by gradually adding a molecule of bromine to one of mesitylene in the dark.[2] It is a liquid, which has a faintly aromatic odour, boils at 227° and solidifies on cooling in crystals, which melt at −1°.

Dibromomesitylene, $C_6HBr_2(CH_3)_3$, was obtained by Fittig and Storer, together with the preceding compound and tribromomesitylene. Schramm found that it is obtained in the pure state when monobromomesitylene is treated in the dark with the calculated amount of bromine. It crystallizes from alcohol in long, brittle needles, melts at 64° and boils at 285°.

Tribromomesitylene, $C_6Br_3(CH_3)_3$, was obtained by Hofmann and Cahours, and is readily formed when three molecules of bromine are added to one molecule of mesitylene in the dark. It is only slightly soluble in boiling alcohol, from which it crystallizes in thin, brittle needles, while it separates from hot benzene, in which it is more readily soluble, in small monosymmetric prisms, melting at 224°.

Monochloropseudocumene, $C_6H_2Cl(CH_3)_3$, has been prepared by Haller from *a*-pseudocumidine by means of Sandmeyer's reaction (Pt. III. p. 264); it forms lustrous scales or plates, melting at 71°—72°.[3]

a-Monobromopseudocumene, $C_6H_2Br(CH_3)_3$, ($CH_3 : CH_3 : CH_3 : Br = 1 : 2 : 4 : 6$), is best obtained by the action of bromine on pseudocumene in the dark. It crystallizes from hot alcohol in large plates, which show a play of colours, melt at 73° (Beilstein and Kögler; Haller; Schramm) and boils at 236°—238°.[4]

s-Monobromopseudocumene (1 : 2 : 4 : 5). A monobromosulphonic acid is formed, together with the dibromosulphonic acid, by the action of sulphuric acid on dibromopseudocumene, and this yields *s*-monobromopseudocumene on heating with hydrochloric acid. It is a liquid boiling at 236°—238° (Jacobsen).

v-Monobromopseudocumene (1 : 2 : 4 : 3), is obtained by the bromination of *a*-pseudocumenesulphonic acid and the decomposition of the product with superheated steam, as an almost odourless liquid, boiling at 226°—229°.[5]

[1] Fittig and Storer, *Ann. Chem. Pharm.* cxlvii. 6.
[2] *Ber. Deutsch. Chem. Ges.* xix. 212. [3] *Ibid.* xviii. 93.
[4] Jacobsen, *ibid.* xix. 1223. [5] Kelbe, *ibid.* xix. 1546.

Dibromopseudocumene, $C_6HBr_2(CH_3)_3$ (1 : 2 : 4 : 5 : 6), is formed, together with the following compound, when pseudocumene is treated with bromine in the dark or in diffused daylight. It is tolerably soluble in alcohol, crystallizes in long, flat, lustrous and very pliant needles, melts at 61·3° (Schramm) and boils at 293°—294° (Jacobsen).

Tribromopseudocumene, $C_6Br_3(CH_3)_3$, is also only slightly soluble in boiling alcohol, and crystallizes when the solution is gradually cooled in very thin, long, pliant needles, melting at 225°—226° (Fittig and Laubinger).

Tribromohemellithene, $CBr_3(CH_3)_3$, crystallizes from hot alcohol in long, fine needles, melting at 245°.[1]

NITROTRIMETHYLBENZENES.

2330 *Mononitromesitylene*, $C_6H_2(NO_2)(CH_3)_3$, was obtained in the impure state by Kane, who overlooked the presence of nitrogen in it and named it mesitaldehyde, C_3H_4O. Cahours and Hofmann also failed to prepare this substance pure. It is formed when mesitylene is heated with nitric acid of sp. gr. 1·38, and in considerable quantity as a by-product in the preparation of mesitylenic acid from which it is separated by means of its greater volatility with steam.[2] It can also be obtained from dinitromesitylene by reducing the latter to nitro-amido-mesitylene, dissolving this in cold alcohol and treating the solution with nitrogen trioxide until the liquid smells distinctly of ethyl nitrite. It is then heated on the water-bath until the evolution of nitrogen ceases, the nitromesitylene precipitated with water and finally distilled with steam.[3]

It is tolerably soluble in cold, in almost every proportion in boiling alcohol, and crystallizes in transparent, lustrous, yellow prisms, which are tolerably thick and often an inch in length, while it sometimes forms large tablets, melts at 44°[4] and boils at 255° (Ladenburg).

Dinitromesitylene, $C_6H(NO_2)_2(CH_3)_3$, which was discovered by Hofmann,[5] is very readily formed when mesitylene is allowed to

[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* xix. 2520.
[2] Fittig and Storer, *Ann. Chem. Pharm.* cxlvii. 1.
[3] Ladenburg, *ibid.* clxxix. 170.
[4] Biedermann and Ledoux, *Ber. Deutsch. Chem. Ges.* viii. 57.
[5] *Ann. Chem. Pharm.* lxxi. 130.

drop into well-cooled, fuming nitric acid ; the solution is poured into cold water after standing for some time, and the curdy precipitate washed with water. It crystallizes from hot alcohol in colourless, lustrous, rhombic, prisms, often an inch in length, which melt at 86°. "The extreme readiness with which mesitylene is completely converted in the cold into this splendid crystalline compound is so characteristic that it affords the best means of detecting the hydrocarbon." [1]

Trinitromesitylene, $C_6(NO_2)_3(CH_3)_3$, was discovered by Cahours,[2] and carefully investigated by Hofmann and Fittig. It is obtained in a similar manner to the dinitro-compound when a mixture of one volume of fuming nitric acid with two volumes of concentrated sulphuric acid is employed, the formation being complete after a few seconds. It is almost insoluble in cold alcohol and very slightly soluble in hot alcohol, from which it crystallizes in fine, white needles, melting at 230°—232°. It separates from hot acetone, in which it is more readily soluble in large, transparent, vitreous prisms, belonging to the asymmetric system.[3]

α-Mononitropseudocumene, $C_6H_2(NO_2)(CH_3)_3$,($CH_3 : CH_3 : CH_3 : NO_2$=1 : 2 : 4 : 5), is readily formed when pseudocumene is dissolved in concentrated nitric acid [4] and crystallizes from alcohol in long, strongly refractive prisms, which melt at 71° and become coloured yellow on exposure to the light. It boils at 265°, and is not further acted upon by nitric acid in the cold, while mesitylene under these conditions is immediately converted into the dinitro-compound.

It is converted by the action of zinc dust on its solution in alcoholic potash into *azopseudocumene*, $C_{18}H_{22}N_2$, which separates from glacial acetic acid in fine, reddish yellow crystals, melts at 173°—174° and is converted by further reduction into the colourless *hydrazopseudocumene*, which melts at 124°—125°.[5]

β-Mononitropseudocumene, (1 : 2 : 4 : 6), has been prepared from *α*-nitropseudocumidine by means of the diazo-reaction, and forms compact prisms, melting at 20°.[6]

γ-Mononitropseudocumene, (1 : 2 : 4 : 3), is obtained in a similar

[1] Fittig, *Ann. Chem. Pharm.* cxli. 132. [2] *Ibid.* lxix. 241.
[3] Bodewig, *Jahresb. Chem.* 1879, 369.
[4] Schaper, *Zeitschr. Chem.* 1867, 12 ; Fittig and Laubinger, *Ann. Chem. Pharm.* cli. 259.
[5] Pospjechow, *Ber. Deutsch. Chem. Ges.* xx. Ref. 217.
[6] Edler, *ibid.* xviii. 629.

manner from γ-nitropseudocumidine, and forms yellow crystals, melting at 30°.[1]

Trinitropseudocumene, $C_6(NO_2)_3(CH_3)_3$, is formed by allowing pseudocumene to drop into a mixture of nitric and sulphuric acids, the liquid being subsequently warmed. It is also very slightly soluble in boiling alcohol, from which it crystallizes in small, colourless needles, united in stellate groups. It crystallizes from hot benzene in hard, tolerably thick, transparent, quadratic prisms, which melt at 185°, and sublime at a higher temperature. These crystals are a very characteristic derivative of pseudocumene; if a mixture of this with mesitylene be nitrated by the method described, the trinitro-compounds can readily be separated by recrystallization from benzene, since the needles of trinitromesitylene can readily be distinguished and mechanically separated from the compact crystals of trinitropseudocumene.[2] According to Engler, who has employed this method to detect these hydrocarbons in rock-oils, a mixture of the trinitrocompounds melts at 167°. In order to decompose this into its constituents, it is heated on the water-bath for several hours with a quantity of alcohol which is insufficient for complete solution, the trinitropseudocumene being dissolved while the trinitromesitylene remains behind. When pseudocumene is boiled with fuming nitric acid, a liquid substance is formed in addition to trinitropseudocumene; this is probably dinitropseudocumene, but could not be obtained in the pure state (Fittig and Laubinger).

Trinitrohemellithene, $C_6(NO_2)_3(CH_3)_3$. The first product of the action of a mixture of nitric and sulphuric acids on hemellithene is a mononitro-derivative, melting at about 100°, which is converted by the further action of the acid, finally assisted by heat into the trinitro-compound. This crystallizes from hot alcohol in compact prisms, which have a vitreous lustre and melt at 209° (Jacobsen).

[1] Mayer, *Ber. Deutsch. Chem. Ges.* xx. 966.
[2] Fittig and Wackenroder, *ibid.* cli. 295.

TRIMETHYLBENZENESULPHONIC ACIDS, $C_6H_2(CH_3)_3SO_3H$.

2331 *Mesitylenesulphonic acid* was first prepared by Hofmann by dissolving mesitylene in fuming sulphuric acid, and was subsequently studied by Fittig, Jacobsen and Rose.[1] It forms rhombic tablets, melts at 77° and contains two molecules of water, which are lost over sulphuric acid. The salts crystallize well.

Mesitylenesulphonic chloride, $C_6H_2(CH_3)_3SO_2Cl$, crystallizes from ether in large, wedge-shaped needles, melting at 57°.[2]

Mesitylenesulphamide, $C_6H_2(CH_3)_3SO_2.NH_2$, is soluble in 3000 parts of water at 0° and in 185 parts of boiling water, from which it crystallizes in long, hair-like needles. It dissolves much more readily in alcohol and is deposited from this solution as a mass, which after drying is fibrous and resembles asbestos, melts at 141°—142° and readily sublimes to a voluminous crystalline mass. On heating to 160°—165° with hydrochloric acid, it decomposes into ammonia, sulphuric acid and mesitylene. This compound may be employed for the separation of mesitylene from pseudocumene, since the sulphamide of the latter is less soluble in water and alcohol.[3] One hundred parts of 83 per cent. alcohol dissolve:

	Mesitylenesulphamide.	Pseudocumenesulphamide.
At 0°	5·55	1·19
At the boiling-point. .	113·65	22·73

Mesitylenedisulphonic acid, $C_6H(CH_3)_3(SO_3H)_2$, is formed by heating mesitylene with ten parts of fuming sulphuric acid to 30°—40° for two or three days, during which time three to four parts of phosphorus pentoxide are added in small quantities every ten hours. It crystallizes in deliquescent needles. The potassium salt, $C_6H(CH_3)_3(SO_3K)_2 + 2H_2O$, decomposes almost quantitatively on heating, mesitylene being formed:[4]

$$C_6H(CH_3)_3(SO_3K)_2 + 2H_2O = C_6H_3(CH_3)_3 + 2SO_4KH.$$

[1] *Ann. Chem. Pharm.* clxiv. 53.
[2] Holtmeyer, *Zeitschr. Chem.* 1867, 686.
[3] Jacobsen, *Ann. Chem. Pharm.* clxxxiv. 184.
[4] Barth and Herzig, *Monatsh. Chem.* i. 808.

α-Pseudocumenesulphonic acid, (CH_3:CH_3:CH_3:SO_3H=1:2:4:5 4:5). The preparation of this substance has already been described. It crystallizes in cubes, is only slightly soluble in dilute sulphuric acid and melts at 111°—112°.[1]

α-Pseudocumenesulphonic chloride, $C_6H_2(CH_3)_3SO_2Cl$, separates from ether in large, transparent, monosymmetric prisms, melting at 61°.[2]

α-Pseudocumenesulphamide, $C_6H_2(CH_3)_3SO_2.NH_2$, dissolves in 7000 parts of cold, and 380 parts of boiling water; it is only slightly soluble in cold, more readily in hot alcohol, from which it crystallizes in short, hard, transparent prisms, which are decomposed by hydrochloric acid at 173°—175° with regeneration of pseudocumene (Jacobsen).

β-Pseudocumenesulphonic acid (1:2:4:6) is obtained by dissolving *α*-bromopseudocumene in fuming sulphuric acid and treating the sodium salt of the bromosulphonic acid with ammonia and zinc dust. Its barium salt is tolerably soluble in water.

β-Pseudocumenesulphamide separates from hot alcohol as a soft crystalline mass, consisting of fine prisms, and crystallizes from a mixture of benzene and alcohol in thick prisms, which melt at 178°—179°.[3]

γ-Pseudocumenesulphonic acid (1:2:4:3) has been prepared from dibromopseudocumenesulphonic acid, and forms a readily soluble sodium salt.

γ-Pseudocumenesulphamide forms small flat needles or plates, melting at about 113° (Jacobsen).

Hemellithenesulphonic acid (1:2:3:5) crystallizes from dilute sulphuric acid in oblique, six-sided tablets, containing water of crystallization, and forms a difficultly soluble barium salt.

Hemellithenesulphamide crystallizes from hot alcohol in short, hard, transparent prisms, which are even less soluble in cold alcohol than pseudocumenesulphamide and melt at 195°. It yields two sulphaminehemellithic acids on oxidation.[4]

[1] Kelbe and Pathe, *Ber. Deutsch. Chem. Ges.* xix. 1546.
[2] Radlof, *ibid.* xi. 32.
[3] Jacobsen, *ibid.* xix. 1218; Kelbe and Pathe, *ibid.* xix. 1546.
[4] Jacobsen, *ibid.* xv. 1858; xix. 2511 and 2517.

TRIMETHYLHYDROXYBENZENES, $C_6H_2(CH_3)_3OH$.

2332 *Mesitol* has been obtained by means of the diazo-reaction from amidomesitylene or mesidine[1] and by fusing mesitylenesulphonic acid with caustic potash.[2] It forms crystals, which smell like phenol and melt at 68°—69°, is readily volatile with steam, boils at 219·5° and gives no colouration with ferric chloride.

Nitromesitol, $C_6H(NO_2)(CH_3)_3OH$, which has been prepared from nitromesidine by means of the diazo-reaction, crystallizes from hot water in yellow plates, which melt at 64° and are readily volatile with steam.

Amidomesitol, $C_6H(NH_2)(CH_3)_3OH$. The hydrochloride of this base, which crystallizes in needles, is formed by the action of tin and hydrochloric acid on nitromesitol; the free base forms crystals, which readily change into a resinous mass.[3]

a-Pseudocumenol ($CH_3 : CH_3 : CH_3 : OH = 1 : 2 : 4 : 5$) is obtained by fusing pseudocumenesulphonic acid with caustic potash,[4] and has also been prepared from *a*-pseudocumidine by means of the diazo-reaction.[5] It forms fine, pliant needles which smell like phenol, melts at 73° (Auwers) and boils at 232°. It gives no colouration with ferric chloride, and on fusion with caustic potash is converted into hydroxy-xylic acid, which decomposes into carbon dioxide and *a*-metaxylenol when heated with lime.

Pseudocumenyl methyl ether, $C_6H_2(CH_3)_3OCH_3$, is formed by heating a solution of *a*-cumidine in methyl alcohol with sulphuric acid and potassium nitrite. It is a liquid, which possesses a pleasant aromatic odour[6] and boils at 209°—211° (Auwers).

Nitro-a-pseudocumenol, $C_6(CH_3)_3H(NO_2)OH$ (1 : 2 : 4 : 3 : 5). When *a*-pseudocuminol is brought into well-cooled, fuming nitric acid, *nitropseudocumenyl nitrate*, $C_6(CH_3)_3H(NO_2)ONO_2$, is formed by a singular reaction. This substance crystallizes

[1] Biedermann and Ledoux, *Ber. Deutsch. Chem. Ges.* viii. 57.
[2] *Ibid.* viii. 250; Jacobsen, *Ann. Chem. Pharm.* cxcv. 265.
[3] Knecht, *Ber. Deutsch. Chem. Ges.* xv. 1375.
[4] Reuter, *ibid.* xi. 29.
[5] Liebermann and Kostanecki, *ibid.* xvii. 885; Auwers, *ibid.* xvii. 2976.
[6] Hofmann *ibid.* xvii. 1918.

from ether in lustrous, rhombic tablets or prisms, which melt at 84° with decomposition and are converted into nitropseudocumenol by evaporation with alcohol on the water-bath. The latter crystallizes in long, reddish yellow needles or prisms, which have a fatty lustre, melt at 48° and are reconverted into the nitrate by heating with dilute nitric acid. This substance is also prepared by the action of nitric acid on pseudocumenyl methyl ether.

Dinitropseudocumenol, $C_6(CH_3)_3(NO_2)_2OH$, is obtained from the metameric nitrate by the action of ammonia, a small amount of nitropseudocumenol and a resinous substance being also formed. It crystallizes from alcohol in yellow, cross-shaped or fascicular groups of needles, melting at 112°.[1] It forms a deep red-coloured solution in alkalis, from which it is reprecipitated by acid.

Amido-a-pseudocumenol, $C_6(CH_3)_3H(NH_2)OH$, is obtained when *a*-cumenol is acted upon by a diazo-salt and the resulting phenylazopseudocumenol, $C_6H_5.N_2.C_6(CH_3)_3H(OH)$, reduced with tin and hydrochloric acid (Liebermann and Kostanecki), and may be obtained in a similar manner from the nitrate described above. It is a crystalline substance, which sublimes in needles, melts at 166°—167° and gives a reddish violet colouration with Liebermann's reagent.

β-Pseudocumenol (1 : 2 : 4 : 6) has been prepared from *β*-pseudocumidine [2] and *β*-pseudocumenesulphonic acid;[3] it forms crystals, melting at 95°, and boils at 230°—231°.

γ-Pseudocumenol (1 : 2 : 4 : 3) has been obtained both from the corresponding pseudocumidine [4] and sulphonic acid (Jacobsen). It crystallizes from ether in long needles, melts at 62° and boils at 232°—234°. It gives no colouration with ferric chloride.

Hemellithenol (1 : 2 : 3 : 5) was prepared by Jacobsen from the sulphonic acid; it crystallizes from alcohol in long, flat needles, melting at 81°, and gives no colouration with ferric chloride.

[1] Auwers, *Ber. Deutsch. Chem. Ges.* xviii. 2655.
[2] Edler, *ibid.* xviii. 629.
[3] Jacobsen, *ibid.* xix. 1218.
[4] Engel, *ibid.* xviii. 2229.

TRIMETHYLDIHYDROXYBENZENES.

2333 *Pseudocumenequinol*, $C_6H(CH_3)_3(OH_2)$. The corresponding quinone is formed by the oxidation of isodurenol,[1] $C_6H(CH_3)_4OH$, and isoduridine,[2] $C_6H(CH_3)_4NH_2$, as an oily yellow liquid, which possesses the characteristic odour of the quinones and solidifies on cooling to a crystalline mass, melting at 11°. It is converted by sulphur dioxide into the quinol, which crystallizes from hot water in splendid white needles, melting at 169°.

Nitropseudocumenequinol, $C_6(NO_2)(CH_3)_3(OH)_2$. When pseudocumenecarboxylic acid, $C_6(CH_3)_3O_2.CO_2H$, is heated with concentrated nitric acid, *nitropseudocumenequinone*, $C_6(NO_2)(CH_3)_3O_2$, is obtained, its formation by this reaction corresponding to that of nitranilic acid from dihydroxyterephthalic acid (Vol. III. Pt. IV. p. 520). The quinone forms golden yellow plates, which melt at 113° and readily sublime, and is converted by sulphur dioxide into the quinol, which crystallizes in long, golden-yellow needles and melts at 106.°[3]

Mesorcinol, $C_6H(CH_3)_3(OH)_2$, is readily formed when amidomesitol hydrochloride is dissolved in water and treated with the theoretical quantity of sodium nitrite at a low temperature; nitrogen is evolved and the reaction must be completed by boiling. Mesorcinol is readily soluble in ether, slightly in cold and readily in hot water, sublimes in dazzling white plates, melting at 149°—150°, and boils at 274°—275°. If its solution be treated with ferric chloride and distilled, hydroxymetaxyloquinone (Vol. III. Pt. IV. p. 404) is formed and can readily be recognized by its characteristic reactions. On heating it with sulphuric acid a colouring-matter is produced, which forms a red solution in alkalis; the dilute rose-red solution shows a deep green fluorescence.[4]

[1] Hofmann, *Ber. Deutsch. Chem. Ges.* xvii. 1916.
[2] Nölting and Baumann, *ibid.* xviii. 1152.
[3] Nef, *Ann. Chem. Pharm.* ccxxxvii. 17.
[4] Knecht, *ibid.* xv. 1375.

AMIDOTRIMETHYLBENZENES.

2334 *Amidomesitylene* or *Mesidine*, $C_6H_2(CH_3)_3NH_2$, is formed by the reduction of nitromesitylene (Fittig and Storer), as well as by heating trimethylphenylammonium iodide to the melting point of lead,[1] and occurs in varying quantities in crude cumidine.[2] It is a liquid which boils at 229°–230°[3] and has almost the same specific gravity as water.

Dimethylmesidine, $C_6H_2(CH_3)_3N(CH_3)_2$, is a liquid, boiling at 213—214°, which does not combine with methyl iodide even at 150° (Hofmann).

Acetmesidide, $C_6H_2(CH_3)_3NH(C_2H_3O)$, crystallizes from hot alcohol in broad prisms, melting at 216°–217°.

Mesitylcarbimide, $C_6H_2(CH_3)_3NCO$. The product of the action of ethylchlorocarbonate or mesidine is *mesitylurethane*, $C_6H_2(CH_3)_3NH.CO.OC_2H_5$, which forms needles, melting at 61°–62° and is converted into mesitylcarbimide by heating with phosphorus pentoxide. This is a liquid, which has a pungent odour, boils at 218° – 220° and becomes turbid after a short time, a gelatinous mass being deposited (Eisenberg).

Mesityl mustard oil, $C_6H_2(CH_3)_3NCS$, was prepared by Eisenberg by heating mesidine with carbon disulphide and alcoholic potash. It crystallizes in long, lustrous needles, which have a faintly pungent odour and melt at 64°.

Nitromesidine, $C_6H(NO_2)(CH_3)_3NH_2$, was obtained by Maule from dinitromesitylene by passing sulphuretted hydrogen into its alcoholic solution.[4] The reaction only proceeds slowly[5] and is not greatly accelerated by the addition of ammonia (Ladenburg). Nitromesidine crystallizes from alcohol in golden yellow needles, which melt at 73° – 74° and are not decomposed by boiling caustic soda.

Nitro-acetmesidide, $C_6H(NO_2)(CH_3)_3NH(C_2H_3O)$, is formed when acetmesidide is heated with nitric acid to which a little water has been added (Ladenburg), or when its solution in

[1] Hofmann, *Ber. Deutsch. Chem. Ges.* v. 715 ; viii. 61.
[2] Eisenberg, *ibid.* xv. 1011 ; *Inauguraldissert. Berlin*, 1882 ; Engel, *Ber. Deutsch. Chem. Ges.* xviii. 2229.
[3] Ladenburg, *Ann. Chem. Pharm.* clxxix. 163.
[4] *Ibid.* xiii. 137.
[5] Biedermann and Ledoux, *Ber. Deutsch. Chem. Ges.* viii. 57 ; Knecht, *ibid.* xv. 1375.

glacial acetic acid is treated with fuming nitric acid (Biedermann and Ledoux). It crystallizes from boiling alcohol in silky needles or small prisms, which melt at 191° and are not decomposed by boiling with alkalis. It is a weak base, which dissolves in concentrated hydrochloric and is reprecipitated by ammonia but not by water alone. It decomposes into acetic acid and nitromesidine when it is heated to 150° with hydrochloric acid.

Dinitromesidine, $C_6(NO_2)_2CH_3)_3NH_2$, was obtained by Fittig by the reduction of trinitromesitylene with ammonium sulphide. It crystallizes from hot alcohol in lustrous, yellow needles, melting at 193°—194°.

Dinitro-acetmesidide, $C_6(NO_2)_2(CH_3)_3NH(C_2H_3O)$, is prepared by dissolving the mononitro-compound in a mixture of nitric and sulphuric acids, and crystallizes from hot alcohol in dazzling white needles, which melt at 275° and are resolved into acetic acid and dinitromesidine by heating with hydrochloric acid (Ladenburg).

Diamidomesitylene, $C_6H(CH_3)_3(NH_2)_2$, is formed by the action of tin and hydrochloric acid on dinitromesitylene (Fittig) and on trinitromesitylene (Ladenburg), ammonia being in this case eliminated. It crystallizes from hot water in hair-like needles and separates from an ethereal solution in transparent, monosymmetric crystals, which melt at 90° and sublime in lustrous needles when carefully heated. Chronic acid solution oxidizes it to hydroxymetaxyloquinone ; its salts crystallize well.

Nitrodiamidomesitylene, $C_6(NO_2)(CH_3)_3(NH_2)_2$, is obtained by the further action of ammonium sulphide on dinitromesidine. It crystallizes from hot water, in which it is only slightly soluble, in large, orange-red plates, and separates from alcohol on the spontaneous evaporation of the solution in very large, well-formed monosymmetric crystals, which are perfectly transparent, possess a diamond lustre and are of nearly the same colour as sodium nitroprusside, this substance being one of the most beautiful of organic compounds. It melts at 184° and is a well characterised base, its hydrochloride, $C_9H_9(NO_2)(NH_2)_2(ClH)_2$, forms colourless or pale yellow, quadratic tablets (Fittig).

2335 *a-Pseudocumidine* ($CH_3 : CH_3 : CH_3 : NH_2 = 1 : 2 : 4 : 5$) was obtained by Schaper by the reduction of *a*-nitropseudocumene. It is manufactured by heating commercial xylidine to 250° with hydrochloric acid and methyl alcohol. The difficultly soluble nitrate of *a*-pseudocumidine is then pre-

pared from the crude cumidine, which contains isomeric bases, and is finally decomposed by caustic soda.[1] The crude cumidine may also be fractionated and the portion boiling between 232°–235° purified by washing with alcohol.[2]

α-Pseudocumidine crystallizes from hot water in long, silky needles, and from alcohol in large, lustrous, transparent prisms, melts at 68° and boils at 234° (Auwers). It is employed in the manufacture of azo-dyes. Its salts crystallize well. On oxidation with potassium ferricyanide it is converted into the azopseudocumene which has been previously mentioned (Pospjechow).

Methylpseudocumidine, $C_6H_2(CH_3)_3NH(CH_3)$, melts at 44° and boils at 237°.

Dimethylpseudocumidine, $C_6H_2(CH_3)_3N(CH_3)_2$, is an oil, which has a pleasant smell of flowers and boils at 222° (Hofmann).

α-Acetpseudocumide, $C_6H_2(CH_3)_3NH(C_2H_3O)$, crystallizes in compact, white needles, melting at 164° (Auwers).

α-Nitropseudocumidine, $C_6H(NO_2)(CH_3)_3NH_2$. When the preceding compound is nitrated, *nitro-acetpseudocumide* is formed and crystallizes in long, yellowish prisms, melting at 202°–204° (Auwers). This is converted by hydrolysis into nitropseudocumidine, which separates from alcohol in large, red, asymmetric crystals, melting at 46°–47°.

α-Diamidopseudocumene, $C_6H(CH_3)_3(NH_2)_2$(1 : 2 : 4 : 5 : 6), has been prepared by the reduction of *α*-nitropseudocumidine. It crystallizes from hot water in colourless needles, melting at about 90°; a very dilute solution of its hydrochloride is coloured deep red by ferric chloride, and the dry, perfectly neutral salt evolves hydrochloric acid when it is heated with benzaldehyde. The base is therefore an orthodiamine (Vol. III. Pt. IV. p. 62), which is also proved by the fact that nitro-acetpseudocumide is converted by reduction into *ethenyldiamidopseudocumene*:

$$C_6H(CH_3)_3\begin{cases}NO_2\\NH.CO.CH_3\end{cases} + 6H = C_6H(CH_3)_3\begin{cases}-N-\\NH\end{cases}\!\!>C.CH_3 + 3H_2O.$$

The compound obtained in this way is not decomposed by boiling alcoholic potash.[3]

[1] Hofmann, *Ber. Deutsch. Chem. Ges.* xvii. 2985.
[2] Auwers, *ibid.* xviii. 2661. [3] Edler, *ibid.* xviii. 629.

α-Dinitropseudocumidine, $C_6(NO_2)_2(CH_3)_3NH_2$. The further nitration of nitro-acetpseudocumide yields dinitro-acetpseudocumide, which melts at 280° and on heating with sulphuric acid is converted into dinitropseudocumidine, which crystallizes from alcohol in long, lustrous, orange-yellow needles, melting at 183°. It has only feeble basic properties and is converted by reduction into a strong base, which has not yet been thoroughly investigated.[1]

Pseudocumylhydrazine, $C_6H_2(CH_3)_3N_2H_3$, is prepared from *α*-cumidine by Fischer's method; it crystallizes from ether in needles, melting at 120°. This compound was prepared in order to determine whether technically prepared cumidine is identical with that obtained from pseudocumene, and for this purpose was converted into the hydrocarbon according to a method proposed by Baeyer. This consists in adding four parts of water to the hydrazine, heating to boiling and gradually adding a 10 per cent. solution of copper sulphate :

$$C_6H_2(CH_3)_3NH.NH_2 + 2CuSO_4 + H_2O = C_6H_3(CH_3)_3 + Cu_2O + N_2 + 2H_2SO_4.$$

Pure pseudocumene was obtained in this way.[2]

β-Pseudocumidine (1 : 2 : 4 : 6) is formed when *β*-nitropseudocumene is reduced with iron filings and acetic acid. It is readily volatile with steam and solidifies in cooling to a crystalline mass, melting at 36°.[3]

γ-Pseudocumidine (1 : 2 : 4 : 3) is contained in crude cumidine. When the fraction boiling at 225°—227° is boiled with glacial acetic acid for twelve hours, the acetyl-compound is formed, which, after being freed by pressure from the unattacked oil, is repeatedly crystallized from alcohol, a small quantity of acetmesidide being first deposited, while a compound is obtained from the mother-liquor, which boils at 112° and yields the new cumidine on distillation with caustic potash.[4] This substance has also been prepared by the reduction of *γ*-nitropseudocumene and is a liquid, boiling at 236° (Mayer).

γ-Nitropseudocumidine, $C_6H(CH_3)_3(NO_2)(NH_2)$(1 : 2 : 4 : 3 : 5), was obtained by Fittig and Laubinger, who reduced trinitropseudocumene with ammonium sulphide. Mayer found that when sulphuretted hydrogen is passed into a boiling solution of

[1] Auwers, *Ber. Deutsch. Chem. Ges.* xviii. 2661.
[2] Haller, *ibid.* xviii. 89.
[3] Edler, *ibid.* xviii. 629.
[4] Engler, *ibid.* xviii. 2229.

trinitropseudocumene in alcoholic ammonia, the acid $C_9H_{12}N_2SO_5$ is first formed. This compound is either a nitrocumidinesulphonic acid, $C_6(CH_3)_3NO_2(NH_2)SO_3H$, or more probably nitrocumene-sulphamic acid, $C_6H(CH_3)_3NO_2(NH.SO_3H)$, since, on heating with water to 180°, it decomposes quantitatively into sulphuric acid and γ-nitropseudocumidine, which is best prepared from trinitropseudocumene in this manner.[1] It crystallizes from boiling water or alcohol in splendid golden-yellow, lustrous needles, melting at 137°, and forms salts, which crystallize well and are difficultly soluble.

	Melting-point.
γ Nitro-acetcumidide, $C_6H(NO_2)(CH_3)_3NH(C_2H_3O)$, dull yellow needles	131°
γ-Dinitro-acetcumidide, $C_6(NO_2)_2(CH_3)_3NH(C_2H_3O)$, colourless needles	204°
γ-Dinitropseudocumidine, $C_6(NO_2)_2NH_2$, fine, yellow needles	78°

γ-Diamidopseudocumene, $C_6H(CH_3)_3(NH_2)_2$, was obtained by Meyer from γ-nitropseudocumidine by reduction with tin and hydrochloric acid. It is readily soluble in benzene and separates on the addition of petroleum-spirit in compact needles, melting at 84°. Its hydrochloride produces a deep yellow colouration in a very dilute solution of sodium nitrite, while a brown precipitate is formed in a stronger solution. It forms chrysoïdines with diazo-salts and therefore contains the amido-groups in the meta-position, this constitution being confirmed by its other reactions.

MESITYL-COMPOUNDS.

2336 *Mesityl alcohol*, $C_6H_3(CH_3)_2CH_2.OH$, has been prepared from its acetic ether and forms a liquid which has a similar smell to benzyl alcohol and boils at 218°—221°.

Mesityl chloride, $C_6H_3(CH_3)_2CH_2Cl$, is formed when mesitylene is chlorinated at a tolerably high temperature, which must not however exceed 215°, and is a liquid boiling at 215°—220°.[2]

Mesityl bromide, $C_6H_3(CH_3)_2CH_2Br$, is obtained by the action of bromine on mesitylene at 135°—140°, and crystallizes in long

[1] *Ber. Deutsch. Chem. Ges.* xx. 966.
[2] Robinet, *Compt. Rend.* xcvi. 500.

needles or prisms, melting at 38°. It boils at 230° and yields a vapour, which produces a copious flow of tears.[1]

Mesityl acetate, $C_6H_3(CH_3)_2CH_2.O.C_2H_3O$, is prepared by heating the chloride or bromide with potassium acetate and acetic acid. It forms a pleasant-smelling liquid, which, according to Wispek, boils at 228°—231°, but according to Robinet at 242°.

Bromomesityl alcohol, $C_6H_2Br(CH_3)_2CH_2.OH$. The bromide of this is formed by the action of bromine on bromomesitylene in the sunlight and is a liquid which decomposes on distillation. When it is boiled with an alcoholic solution of potassium acetate and the product decomposed with caustic potash, the alcohol is obtained. It crystallizes from petroleum-spirit in stellate groups of needles, which melt at 66°—66·5° and are oxidized to β-bromomesitylenic acid by potassium permanganate. It decomposes on distillation with formation of bromomesitylene, β-bromomesitylaldehyde, which rapidly oxidizes in the air, and other products. The main reaction is explained by the following equation :[2]

$$2C_6H_2Br(CH_3)_2CH_2.OH = C_6H_2Br(CH_3)_3 + C_6H_2Br(CH_3)CHO + H_2O.$$

DIMETHYLBENZENECARBOXYLIC ACIDS, $C_6H_3(CH_3)_2CO_2H$.

2337 The numbers appended give the positions of the side chains in the following order, $CH_3 : CH_3 : CO_2H$.

Mesitylenic acid, (1 : 3 : 5), was first prepared by Fittig. Mesitylene is boiled for 16—20 hours with nitric acid of sp. gr. 1·4, to which two volumes of water have been added, and the product is then greatly diluted with water and submitted to distillation. Nitromesitylene passes over first and then the acid, the distillation being continued until crystals of this are no longer deposited in the condenser, water being added to the residue in the retort as often as is necessary. The acid is then filtered off and the filtrate saturated with sodium carbonate, evaporated to a small bulk, and precipitated with hydrochloric acid. The acid thus obtained is added to that remaining on the filter, which forms the larger portion, and the whole is boiled for

[1] Wispek, *Ber. Deutsch. Chem. Ges.* xvi. 1577.
[2] Schramm, *ibid.* xix. 212.

some time with tin and concentrated hydrochloric acid in order to remove any nitro-compounds. After cooling it is washed with water, dissolved in sodium carbonate and liberated by the addition of hydrochloric acid to the solution at the boiling-point. The pure mesitylenic acid separates out on cooling in dazzling white crystals.[1]

Uvitic acid, $C_6H_3(CH_3)(CO_2H)_2$, is also a product of this reaction, but is not volatile with steam; in order to isolate this, the filtered oxidation-product is separated from unattacked mesitylene and nitromesitylene by solution in sodium carbonate, the two acids precipitated from the filtrate with hydrochloric acid, treated with tin and hydrochloric acid and finally separated by distillation with water.[2]

According to Remsen and Broun, it is better to employ a mixture of one volume of nitric acid of sp. gr. 1·35 with two volumes of water in this reaction.[3]

Mesitylenic acid is also formed by the oxidation of mesityl alcohol, an oily liquid being obtained at the same time, which forms a crystalline compound with acid sodium sulphite, and is therefore probably *mesitylaldehyde*,[4] $C_6H_3(CH_3)_2CHO$.

Geuther and Fröhlich found that small quantities of mesitylenic acid are formed, together with butyric acid, diethylacetic acid and tri-ethenylbutyric acid, $C_3H_4(C_2H_3)_3CO_2H$, when a mixture of sodium ethylate and sodium acetate is heated with carbon monoxide or zinc dust.[5]

Mesitylenic acid is only soluble to a very small extent in cold water and with difficulty in boiling water, from which it crystallizes in fine, small needles. It separates from alcohol, in which it is very readily soluble, in large, well-developed, monosymmetric crystals, while if boiling water be added to the dilute alcoholic solution until a permanent turbidity is produced, the acid crystallizes on cooling in broad plates and needles, which closely resemble those of benzoic acid. It melts at 166° according to Fittig,[6] while Jacobsen gives 169° as the melting-point, but sublimes below this temperature. Its salts have been examined by Fittig and by Fittig and Brückner.[7]

Calcium mesitylenate, $(C_9H_9O_2)_2Ca$, is scarcely more soluble in hot water than in cold and separates in crystalline crusts when the solution is evaporated.

[1] *Ann. Chem. Pharm.* cxli. 144.
[2] Fittig and Furtenbach, *ibid.* cxlvii. 295.
[3] *Amer. Chem. Journ.* iii. 216.
[4] Robinet, *Compt. Rend.* xcvi. 500.
[5] *Ann. Chem. Pharm.* ccii. 305.
[6] *Ber. Deutsch. Chem. Ges.* xi. 2054.
[7] *Ann. Chem. Pharm.* cxlvii. 45.

Barium mesitylenate, $(C_9H_9O_2)_2Ba$, is more readily soluble in hot water than in cold and does not crystallize immediately when the boiling, saturated solution is allowed to cool, but only after standing for some hours; it forms prisms with a silky lustre.

Ethyl mesitylenate, $C_9H_9O_2.C_2H_5$, is formed by the action of hydrochloric acid on a solution of the acid in absolute alcohol, and is a liquid which has a peculiar, but pleasant, smell resembling that of attar of roses, boils at 241° and solidifies to a crystalline mass below 0°.

Mesitylenamide, $C_6H_3(CH_3)_2CO.NH_2$. The acid chloride is formed by the action of phosphorus chloride on mesitylenic acid, but has not yet been prepared pure. It is converted by ammonia into the amide, which crystallizes from boiling water in needles, which melt at 133° and sublime at a slightly higher temperature (Fittig and Brückner).

2338 *Xylic acid*, (1 : 3 : 4), was first prepared by Kekulé by the action of carbon dioxide and sodium on *a*-bromometaxylene.[1] It may also be obtained, together with paraxylic acid and xylidic acid, by the oxidation of pseudocumene with dilute nitric acid,[2] and is very readily formed when carbonyl chloride is passed into a mixture of metaxylene and aluminium chloride, which is heated to 100° at intervals. The acid chloride is thus formed and is then decomposed with water, the product being subsequently distilled. Unattacked metaxylene passes over first and is followed by an oily liquid, boiling between 170° and 320°, which is extracted with caustic soda, the xylic acid being precipitated from the solution with hydrochloric acid and recrystallized from alcohol.[3] It is also formed when the potassium salt of a-metaxylenesulphonic acid is fused with sodium formate.[4]

Xylic acid is almost insoluble in cold and only slightly soluble in boiling water, and crystallizes from alcohol in well-formed, transparent, monosymmetric prisms, melting at 126°. It boils at 267° under a pressure of 727 mm., and yields pure metaxylene when heated with lime at a comparatively low temperature.

Calcium xylate, $(C_9H_9O_2)Ca + 2H_2O$, is readily soluble in water

[1] *Ann. Chem. Pharm.* cxxxvii. 186.
[2] Schaper, *Zeitschr. Chem.* 1867, 12; 1868, 545; Fittig and Laubinger, *ibid.* cli. 269.
[3] Ador and Meier, *Ber. Deutsch. Chem. Ges.* xii. 1968.
[4] Jacobsen, *ibid.* xi. 18.

and crystallizes in hard, transparent, monosymmetric prisms, which only redissolve very slowly.

Barium xylate, $(C_9H_9O_2)_2Ba$, crystallizes from a concentrated solution in hard, thick plates.

Xylyl chloride, $C_6H_3(CH_3)_2COCl$, is prepared by fusing the acid with phosphorus chloride; it boils at 234°—236°, and solidifies on cooling in fascicular groups of needles, melting at 25·5°.

Xylamide, $C_6H_3(CH_3)_2CO.NH_2$, is obtained by triturating the chloride with ammonium carbonate. It crystallizes from hot water in fan-shaped groups of needles, and from alcohol in prismatic clusters of needles, melting at 181°.

Paraxylic acid, (1 : 2 : 4), is formed by the oxidation of pseudocumene and also when potassium orthoxylenesulphonate is fused with sodium formate (Jacobsen). In order to prepare it, pseudocumene is boiled for about a day with dilute nitric acid, distilled with steam and the distillate neutralized with carbonate of soda and freed from nitropseudocumene by distillation. The residue is then heated with an excess of hydrochloric acid and tin, the acids converted into the calcium salts and these separated by crystallization.

Paraxylic acid is scarcely soluble in water in the cold, and only dissolves to a small extent at the boiling-point; it is deposited from an alcoholic solution, which is allowed to evaporate spontaneously, in concentrically-grouped prisms, melting at 166°. On distillation with lime it yields pure orthoxylene, which was discovered in this way.

Calcium paraxylate, $2(C_9H_9O_2)_2Ca + 7H_2O$, is less soluble in water than calcium xylate, and crystallizes in pointed, white needles, which however redissolve much more rapidly than those of the latter salt.

Barium paraxylate, $(C_9H_9O_2)_2Ba + 4H_2O$, is less soluble in water than barium xylate and crystallizes in fascicular or stellate groups of hard needles.

Isoxylic acid (1 : 4 : 2) was obtained by Jacobsen by heating bromoparaxylene with sodium amalgam and ethyl chlorocarbonate. It crystallizes from alcohol in stellate groups of large needles, melts at 132° and boils at 268°.

Calcium isoxylate, $(C_9H_9O_2)_2Ca + 2H_2O$, is scarcely more soluble in hot water than in cold, and separates on evaporation in tolerably hard, radiating crusts.

Barium isoxylate, $(C_9H_9O_2)_2Ba + 4H_2O$, crystallizes slowly

from a concentrated solution in masses composed of small needles.

Isoxylamide, $C_6H_3(CH_3)_2CO.NH_2$, has been prepared from the chloride, which crystallizes in the cold, by trituration with ammonium carbonate, and is deposited from hot water in long brittle needles, melting at 186°.[1]

v-Xylic acid (1 : 3 : 2) is formed when the potassium salt of *v*-metaxylenesulphonic acid is fused with sodium formate. It is more readily soluble in water than xylic and mesitylenic acids, which also contain the methyl groups in the meta-position, and crystallizes in short needles, melting at 97°—99°.[2]

Hemellithic acid (1 : 2 : 3) is obtained by the oxidation of hemellithene with dilute nitric acid. It is readly volatile with steam and crystallizes from hot alcohol in large, brittle, vitreous prisms, which melt at 144° and are only slightly soluble even in hot water.

Calcium hemellithate, $(C_9H_9O_2)_2Ca + H_2O$, crystallizes from hot water in tufts of prisms and yields pure orthoxylene on distillation with lime.

SUBSTITUTION PRODUCTS OF THE DIMETHYLBENZENECARBOXYLIC ACIDS.

2339 *β-Chloromesitylenic acid*, $C_6H_2Cl(CH_3)_2CC_2H$, is formed by the oxidation of chloromesitylene with dilute nitric acid. It is slightly soluble in hot water, readily in alcohol, from which it crystallizes in monosymmetric prisms, which become coloured brown at 220° without melting.[3]

a-Bromomesitylenic acid, $C_6H_2Br(CH_3)_2CO_2H$, is the chief product of the action of bromine on mesitylenic acid in the cold, and has also been prepared from *a*-amidomesitylenic acid by means of the diazo-reaction. It crystallizes from hot water in fine needles, often an inch in length, and is deposited on the evaporation of its alcoholic solution in large, rhombic prisms, which melt at 146°—147°, solidify at 131° when gradually cooled, and then melt at 137°—138°. It resembles *β*-nitromesitylenic

[1] *Ber. Deutsch. Chem. Ges.* xiv. 2110. [2] Jacobsen, *ibid.* xi. 21.
[3] Fittig and Hoogewerff, *Ann. Chem. Pharm.* cl. 325.

acid in this respect, the lower melting substance being the mobile modification, the higher melting the stable.[1]

β-Bromomesitylenic acid is formed in small quantity together with the *α*-acid, and may also be obtained by the oxidation of bromomesitylene with chromic acid solution or dilute nitric acid.[2] In addition to these methods it has been prepared from *β*-amidomesitylenic acid (Schmitz). It separates from hot water, in which it is only slightly soluble, in compact crystals and from alcohol in well-developed, monosymmetric prisms, which have almost precisely the same form as *β*-nitromesitylenic acid and melt at 214°—215°.

α-Nitromesitylenic acid, $C_6H_2(NO_2)(CH_3)_2CO_2H$, is formed as the chief product, together with the *β*-compound, when mesitylenic acid is brought into fuming nitric acid, the mixture of the two acids being soon deposited. They are converted into their barium salts, that of the *β*-acid crystallizing out almost completely when its hot solution is allowed to cool. The salt of the *α*-acid is obtained from the mother-liquor and is purified by recrystallization and decomposed with hydrochloric acid.

α-Nitromesitylenic acid crystallizes from hot water, in which it is only slightly soluble, in long fine needles, and separates from an alcoholic solution in larger crystals, which form intersecting twins and melt at 210°—212° (Schmitz).

β-Nitromesitylenic acid is also formed, together with nitromesitylene, in the preparation of mesitylenic acid (Fittig and Brückner), as well as by the oxidation of nitromesitylene with chromic acid.[3] It is almost insoluble in cold, only very slightly soluble in boiling water and crystallizes from hot alcohol in well-developed monosymmetric prisms, which, according to Schmitz, commence to soften at 195°, but are not completely fused until the temperature reaches 220·5°. When gradually cooled the acid solidifies at 161°—162° and then melts completely at 167°—168°; if it be now further heated and a crystal of the acid added to the fused mass, it solidifies immediately and does not completely fuse again until the temperature is raised to 220·5°. It therefore exists in two modifications, one of which gradually changes into the other as the temperature is raised. Jacobsen found that the acid obtained by crystallization from hot water or alcohol, or by the evaporation of its solution in absolute

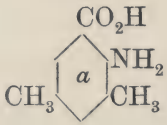
[1] Schmitz, *Ann. Chem. Pharm.* cxciii. 160.
[2] Fittig and Storer, *ibid.* cxlvii. 8.
[3] Emersen, *Amer. Chem. Journ.* viii. 268.

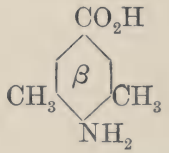
alcohol, melts at 179°, while it separates from hot absolute alcohol in crystals, which melt at 223° and are converted by hot water into the modification which has the lower melting point.[1]

Nitroxylic acid, $C_6H_2(NO_2)(CH_3)_2CO_2H$, was prepared by Schaper by the oxidation of mononitropseudocumene with chromic acid solution. It crystallizes in fine needles, which melt at 195° and are only slightly soluble in cold, more readily in boiling water and readily in alcohol.[2]

2340 *α-Amidomesitylenic acid*, $C_6H_2(NH_2)(CH_3)_2CO_2H$, is obtained by the reduction of the nitro-acid with tin and hydrochloric acid. It crystallizes from hot water or alcohol in long needles, melting at 190°. On heating with lime, it decomposes into carbon dioxide and a-metaxylidine.

β-Amidomesitylenic acid is only slightly soluble in water and crystallizes from hot alcohol in needles, melting at 235°. When heated with lime it yields v-metaxylidine. The constitution of the amidomesitylenic acids is therefore expressed by the following formulae :





The constitution of nitromesitylenic acid and bromomesitylenic acid is also thus determined, and it follows from these, that when a substituted mesitylene is oxidized, the methyl group, which is in the para-position to the substituent, is converted into carboxyl, while when one of the hydrogen atoms in mesitylenic acid is replaced by bromine or nitroxyl, the latter take the ortho-position to the carboxyl.

Sulphomesitylenic acid, $C_6H_2(SO_3H)(CH_3)_2CO_2H$, is formed by the action of sulphur trioxide on mesitylenic acid in two modifications, which can be separated by means of their calcium salts.[3]

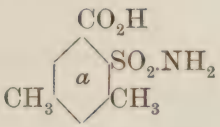
α-Sulphamidomesitylenic acid, $C_6H_2(SO_2.NH_2)(CH_3)_2CO_2H$, is obtained, together with a small amount of the β-acid, by the oxidation of mesitylenesulphamide with chromic acid. It

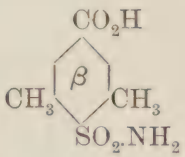
[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* xi. 2052.
[2] *Zeitschr. Chem.* 1867, 13.
[3] Remsen and Brown, *Amer. Chem. Journ.* iii. 218.

crystallizes from hot water or alcohol in short, compact prisms with a vitreous lustre, which melt at 263° and are converted by concentrated HCl at 200° into mesitylenic acid, which is also formed, together with *α*-metaxylenesulphamide, when the sulphamic acid is fused with caustic soda.

β-Sulphamidomesitylenic acid is formed, together with about an equal quantity of the *α*-acid, by the oxidation of mesitylenesulphamide with an alkaline solution of potassium permanganate. It crystallizes from hot water in long fine needles, which are readily soluble in alcohol and melt at 276° with decomposition. On heating with hydrochloric acid, it yields mesitylenic acid and is converted into *β*-hydroxymesitic acid by fusion with caustic soda (Jacobsen).

The constitution of these two acids is expressed by the following formulae :





Sulphamidoxylic acid, $C_6H_2(CH_3)_2(SO_2.NH_2)CO_2H(1:3:4:6)$, is formed by the oxidation of pseudocumenesulphamide. It is almost insoluble in cold water and only slightly soluble in boiling water, from which it crystallizes in long, fine needles which melt at 260° and are converted into xylic acid by hydrochloric acid at 210°.[1]

α-Sulphamidohemellithic acid (1 : 2 : 5 : 3) is obtained, accompanied by the *β*-compound, when hemellithenesulphamide is oxidized with potassium permanganate in faintly alkaline solution, and crystallizes from water in long, flat needles, melting at 238°. On heating to 150° with hydrochloric acid, hemellithic acid is formed.

β-Sulphamidohemellithic acid (1 : 3 : 5 : 2) is more readily soluble than the *α*-acid and crystallizes in stellate groups of microscopic needles, which melt at 174°. An isomeric hemellitic acid is not formed on heating with hydrochloric acid, but decomposition into carbon dioxide and metaxylene takes place.[2]

[1] Jacobsen and Meyer, *Ber. Deutsch. Chem. Ges.* xvi. 190.
[2] Jacobsen, *ibid.* xix. 2519.

DIMETHYLHYDROXYBENZENECARBOXYLIC ACIDS, $C_6H_2(OH)(CH_3)_2CO_2H$.

2341 The numbers appended give the positions of the side chain in the order $CH_3 : CH_3 : CO_2H : OH$.

α-Hydroxymesitylenic acid (1 : 3 : 5 : 6) is formed by fusing mesitylenesulphonic acid with caustic potash,[1] mesitol being first formed and then undergoing oxidation.[2] If the temperature be rapidly raised until the point is reached at which the potassium salt of mesitol floats on the surface of the fused mass, this is almost the only product; while if the separation of the potassium salt be prevented by constant agitation and the maintenance of a lower temperature, the mesitol is oxidized to hydroxymesitylenic acid as rapidly as it is formed.[3]

It may also be obtained by gradually adding potassium nitrite to a solution of *α*-amidomesitylenic acid in dilute sulphuric acid and distilling with steam.[4] It is, however, best prepared by the action of sodium and carbon dioxide on *α*-metaxylenol, which must be diluted with a hydrocarbon of high boiling point in order to prevent the solidification of the mixture.[5]

It is slightly soluble in water, readily in alcohol and crystallizes from dilute alcohol in long, flat needles, which melt at 179°, sublime readily and are volatile with steam. It corresponds to salicylic acid and its aqueous solution is coloured deep blue by ferric chloride. On heating with concentrated hydrochloric acid to 200°, or when rapidly fused with caustic potash at a high temperature, it decomposes into carbon dioxide and *α*-metaxylenol.

β-Hydroxymesitylenic acid (1 : 3 : 5 : 2) is readily formed when *β*-sulphamidomesitylenic acid is fused with potash.[6] It is also formed by the action of nitrous acid on *β*-amidomesitylenic acid, and in small quantity, together with the *α*-acid, by the fusion of mesitylene with caustic potash (Jacobsen).

It crystallizes from hot water, in which it is only slightly soluble, in long, hair-like, pliant needles and from alcohol in shorter compact needles, which melt at 223° and sublime when

[1] Fittig and Hoogueneff, *Ann. Chem. Pharm.* cl. 329.
[2] Jacobsen, *ibid.* cxcv. 274.
[3] Jacobsen, *ibid.* ccvi. 200.
[4] Jacobsen, *Ber. Deutsch. Chem. Ges.* xi. 2055.
[5] Jacobsen, *ibid.* xiv. 44.
[6] Jacobsen, *ibid.* xii. 606.

carefully heated above this temperature. It is not volatile with steam and gives no colouration with ferric chloride ; if the latter be added to a solution of the ammonium salt, however, a brown precipitate is formed, which is soluble in hot water and in an excess of ferric chloride. On heating to 200° with concentrated hydrochloric acid, it decomposes into *v*-metaxylenol and carbon dioxide.

Hydroxyparaxylic acid (1 : 2 : 4 : 5) is formed by the continued fusion of pseudocumene with caustic potash. It is almost insoluble in cold water, only slightly soluble in boiling water, and crystallizes from the latter or dilute alcohol in feathery groups of needles, while it separates from stronger alcohol in very small prisms, which melt at 199° and sublime even below this temperature. It volatilizes slowly with steam and gives a deep bluish-violet colouration with ferric chloride. It is resolved into carbon dioxide and *a*-orthoxylenol by hydrochloric acid at 220°—225°.[1]

Xyletic acid has been prepared by the action of carbon dioxide and sodium on crude xylenol. It forms crystals, melting at 155°, and gives a violet colouration with ferric chloride.[2]

DIMETHYLDIHYDROXYBENZENECARBOXYLIC ACIDS, $C_6H(OH)_2(CH_3)_2CO_2H$.

2342 Only one of these bodies has hitherto been prepared.

Metaxylorcinolcarboxylic acid (1 : 3 : 4 : 6 : 5) is formed when metaxylorcinol (Vol. III. Pt. IV. p. 402) is heated to 130° with a solution of sodium carbonate. It is only slightly soluble in water and crystallizes from dilute alcohol in prisms, which melt at 196° with evolution of carbon dioxide. It gives a deep blue colouration with ferric chloride,[3] and therefore probably contains the hydroxyl in the ortho-position to the carboxyl group, a supposition which is favoured by the readiness with which it decomposes on heating.

[1] Reuter, *Ber. Deutsch. Chem. Ges.* xi. 30 ; Jacobsen, *ibid.* xii. 434.
[2] Wroblewsky, *Zeitschr. Chem.* 1868, 233.
[3] Kostanecki, *Ber. Deutsch. Chem. Ges.* xix. 2323.

MESITENE-COMPOUNDS.

2343 *Mesitene alcohol* or *Mesityleneglycol*, $C_6H_3(CH_3)(CH_2.OH)_2$, is prepared by boiling its chloride for some time with water and lead carbonate. It is a viscid liquid, which has a bitter taste, boils with partial decomposition at 280°, is readily soluble in alcohol and dissolves in about 20 parts of water.[1]

Mesitene chloride, $C_6H_3(CH_3)(CH_2Cl)_2$, is formed, together with mesityl chloride, by the action of chlorine on heated mesitylene. It crystallizes in small plates or needles, melts at 41·5°, and boils at 260°—265°.

Mesitene bromide, $C_6H_3(CH_3)(CH_2Br)_2$, is obtained by the action of bromine on mesitylene vapour, as well as of hydrobromic acid on the glycol, and crystallizes in fine needles, which melt at 66·3°[2] and have a very pungent odour.

Mesitene acetate, $C_6H_3(CH_3)(CH_2.O.C_2H_3O)_2$, is obtained by boiling the chloride with acetic acid and silver acetate as a colourless, almost odourless liquid, which has an unpleasant burning taste and boils at 244° under a pressure of 120 mm.

PSEUDOCUMYLENE COMPOUNDS.

2344 *Pseudocumylene alcohol*, $C_6H_3(CH_3)(CH_2.OH)_2$ (1 : 2 : 4). When pseudocumene is heated with bromine in the sunlight, *pseudocumyl bromide*, $C_6H_3(CH_3)_2CH_2Br$, is the first product. It is a liquid, which is completely decomposed by distillation, and is converted by the further action of bromine into *pseudocumylene bromide*,[3] $C_6H_3(CH_3)(CH_2Br)_2$, which is also formed when pseudocumene is acted upon by bromine at a temperature of 140°.[4] It crystallizes from ether or petroleum-spirit in flat, lustrous needles, melting at 97·5°. On boiling with a solution of

[1] Robinet and Colson, *Compt. Rend.* xcvi. 1863.
[2] Robinet, *ibid.* xcvi. 500.
[3] Schramm, *Ber. Deutsch. Chem. Ges.* xix. 217.
[4] Hjelt and Gadd, *ibid.* xix. 867.

sodium carbonate it is converted into the alcohol, which is only slightly soluble in ether, readily in water, and is oxidized by chromic acid to β-xylidic acid (Hjelt and Gadd).

METHYLBENZENEDICARBOXYLIC ACIDS, $C_6H_3(CH_3)(CO_2H)_2$.

2345 *Uvitic aid*, (1 : 3 : 5), was first prepared by Finkh by boiling pyroracemic or pyruvic acid, $CH_3.CO.CO_2H$, with baryta water.[1] Fittig and Furtenbach then found *mesidic acid* among the oxidation products of mesitylene and stated that it was most probably identical with uvitic acid,[2] this being confirmed by Baeyer.[3] The formation of uvitic acid from pyroracemic acid is not brought about by a simple reaction; Finkh obtained oxalic acid and the syrupy uvitonic acid as by-products, the latter being, according to Böttinger, a badly characterized compound and probably impure. The latter chemist found that in addition to these substances, acetic acid, pyrotartaric acid and uvic acid, $C_7H_8O_3$, are also formed.[4] Since acetone is so readily converted into mesitylene with elimination of water, it was to be expected that pyroracemic acid would be converted by an analagous reaction into trimesic acid, $C_6H_3(CO_2H)_3$, but not a trace of this compound is formed.[5] Harrow subsequently proved that uvic acid is identical with the pyrotritaric acid, which is formed by the dry distillation of tartaric acid (Vol. III. Pt. II. p. 222), and which he prepared synthetically by converting sodium aceto-acetic ether by the action of iodine into diacetosuccinic ether, which yields the ether of uvic acid when boiled with dilute sulphuric acid:

$$\begin{array}{l} CH_3—CO—CH—CO_2 \,.\, C_2H_5 \\ \qquad\qquad\quad | \\ CH_3—CO—CH—CO_2 \,.\, C_2H_5 \end{array} =$$

$$\begin{array}{l} CH_3—CO—CH—CO_2 \,.\, C_2H_5 \\ \qquad\qquad\quad | \\ CH_2{=}C{=}CH \end{array} + CO_2 + C_2H_6O.$$

[1] *Ann. Chem. Pharm.* cxxii. 182.
[2] *Zeitschr. Chem.* [2] iv. i.; *Ann. Chem. Pharm.* cxlvii. 292.
[3] *Zeitschr. Chem.* [2] iv. 119.
[4] *Ann. Chem. Pharm.* clxxii. 239; clxxxviii. 293.
[5] Fittig and Böttinger, *Ber. Deutsch. Chem. Ges.* v. 956.

The formation of uvitic acid from pyroracemic acid is then explained by the following equation :[1]

$$\begin{array}{l} CH_3—CO—CO_2H \\ CH_3—CO—CO_2H \end{array} \quad \begin{array}{l} CO—CO_2H \\ | \\ CH_3 \end{array} \quad = \quad \begin{array}{l} CH_3—CO—CH—CO_2H \\ \quad\quad\quad\quad | \\ CH_2=C=CH \end{array} \quad + 2CO_2 + 2H_2O.$$

Uvitic acid is converted into benzoic acid on fusion with caustic potash by a reaction which can be simply explained by means of the formula given above.

At least four molecules of pyroracemic acid take part in the formation of uvitic acid :

$$\begin{array}{l} \quad\quad CH_3 \\ CO_2H—CO \\ \quad\quad CH_3 \\ \quad\quad CO \\ \quad\quad CO_2H \end{array} \quad \begin{array}{l} CO—CO_2H \\ | \\ CH_3 \\ CO—CO_2H \\ | \\ CH_3 \end{array} \quad = \quad \begin{array}{l} \quad CH_3 \\ \quad | \\ \quad C—CH \\ \quad \| \quad \| \\ HC \quad C—CO_2H \\ \quad | \quad | \\ \quad HC=CH \\ \quad | \\ \quad CO_2H \end{array} + CHO—CO_2H + CO_2 + 3H_2O.$$

The glyoxylic acid, which is simultaneously formed, is decomposed by the baryta into oxalic acid and glycolic acid. The latter has hitherto not been detected among the products of the reaction, but is undoubtedly contained in the so-called uvitonic acid.

The preparation of uvitic acid from mesitylene has already been described in connection with mesitylenic acid. It is almost insoluble in cold water and only very slightly soluble in boiling water, from which it crystallizes in fascicular

[1] *Ann. Chem. Pharm.* cci. 163.

groups of fine needles, while it separates from alcohol in indistinct groups of crystals, and is precipitated from the hot alcoholic solution by the addition of water as a crystalline powder. It melts at 286°—287° and sublimes at a higher temperature without blackening; when a mixture of the calcium salt with half its weight of slaked lime is heated to the melting point of lead, metatoluic acid is formed.[1] Its salts are soluble in water and for the most part crystallize well.

α-Nitro-uvitic acid, $C_6H_2(NO_2)CH_3(CO_2H)_2$, is formed, together with a smaller quantity of the *β*-acid, when uvitic acid is nitrated, and crystallizes in needles or prisms, which melt at 226°—227° and are only slightly soluble in hot water.

β-Nitro-uvitic acid is very slightly soluble in cold, more readily in hot water and crystallizes in acute rhombohedra.

α-Amido-uvitic acid, $C_6H_2(NH_2)CH_3(CO_2H)_2$, crystallizes from alcohol in long, yellow needles; its alcoholic solution has a blue fluorescence.

β-Amido-uvitic acid forms long, light-yellow needles.[2]

Sulpho-uvitic acid, $C_6H_2(SO_3H)CH_3(CO_2H)_2$, is formed when sulphamido-uvitic acid is repeatedly evaporated with hydrochloric acid, and crystallizes from water, which contains sulphuric acid, in small, compact needles (Jacobsen).

Sulphamine-uvitic acid, $C_6H_2(SO_2.NH_2)CH_3(CO_2H)_2$, is formed by the oxidation of mesitylenesulphamide or of the two sulphamidomesitylenic acids with potassium permanganate.[3] It is separated from its salts by the addition of acids as the anhydride, in a similar manner to orthosulphamidobenzoic acid (Vol. III. Pt. IV. p. 268). This crystallizes from hot water in small prisms, which melt at 270°—272°.

2346 *α-Xylidic acid* (2 : 1 : 4) is formed by the oxidation of pseudocumene, and therefore by that of xylic acid and paraxylic acid, with dilute nitric acid. It is liberated from its salts by acids as an amorphous voluminous mass, which is only very slightly soluble in boiling water and separates from the solution in semi-crystalline flocks, while it may be obtained in the form of granular, crystalline, warty masses by the evaporation of its alcoholic solution. It melts at 291° and sublimes in a slow current of carbon dioxide in small, hard needles. The salts do not crystallize well.[4]

[1] Böttinger and Ramsay, *Ann. Chem. Pharm.* clxviii. 255.
[2] Böttinger, *ibid.* clxxxix. 171.
[3] Hall and Remsen, *Amer. Chem. Journ.* ii. 136; Jacobsen, *Ann. Chem. Pharm.* ccvi. 180.
[4] Fittig and Laubinger, *ibid.* cli. 269.

Sulphamidoxylidic acid, $C_6H_2(CH_3)(SO_2.NH_2)(CO_2H)_2$, is formed by the oxidation of sulphamidoxylic acid with potassium permanganate. It is readily soluble in water and crystallizes in needles or prisms, which melt at 295°—300° with decomposition.[1]

β-Xylidic acid (1 : 2 : 4) has been prepared by Jacobsen by the oxidation of isoxylic acid and crystallizes from hot water in microscopic needles, which melt between 320° and 330° and sublime in small crystals with a vitreous lustre.[2]

The *isoxylidic acid*, which Senhofer prepared by fusing γ-toluenedisulphonic acid with sodium formate,[3] and the *methylisophthalic acid*, which is formed by the oxidation of paraxylylmethylketone, $(CH_3)_2C_6H_3.CO.CH_3$, and of methylpropylacetylbenzene, $(CH_3)(C_3H_7)C_6H_3.C.COH_3$, are probably identical with β-xylidic acid.[4]

METHYLHYDROXYBENZENEDICARBOXYLIC ACIDS, $C_6H_2(OH)(CH_3)(CO_2H)_2$.

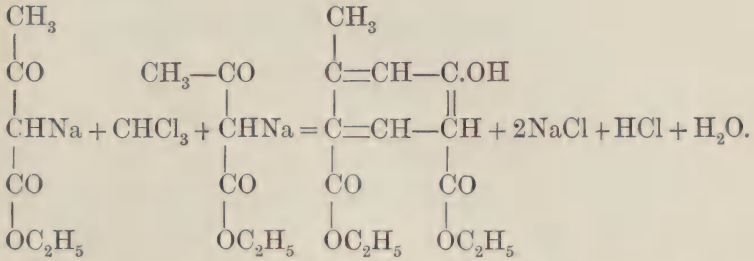
2347 *Di-orthohydroxyuvitic acid* ($CH_3 : CO_2H : CO_2H : OH$ = 1 : 3 : 5 : 4) is prepared by fusing mesitol or *a*-hydroxymesitylenic acid with caustic potash, and crystallizes from hot water in long needles, which become soft between 225°—235° and melt with decomposition. Its aqueous solution gives a fine cherry-red colouration with ferric chloride; when it is heated with hydrochloric acid to 200°, paracresol is formed.[5]

Para-orthohydroxyuvitic acid (1 : 3 : 5 : 2) is obtained by the action of nitrous acid on *a*-amido-uvitic acid,[6] and by fusing sulphamido-uvitic acid with caustic potash.[7] It crystallizes from alcohol in needles, melting with decomposition at about 280°, is very slightly soluble in water and gives a violet-red colouration with ferric chloride. Orthocresol is formed when it is heated with hydrochloric acid.

Metahydryoxyuvitic acid (1 : 4 : 6 : 3). The ethyl ether of this acid is formed by the action of chloroform, chloral, or ethyl-

[1] Jacobsen and Mayer, *Ber. Deutsch. Chem. Ges.* xvi. 190.
[2] *Ibid.* xiv. 2112. [3] *Ann. Chem. Pharm.* clxiv. 134.
[4] Claus, *Ber. Deutsch. Chem. Ges.* xviii. 1858; xix. 233.
[5] Jacobsen, *Ann. Chem. Pharm.* cxcv. 285; ccvi. 193.
[6] Böttinger, *ibid.* clxxxix. 147.
[7] Jacobsen, *ibid.* ccvi. 187; Remsen and Hall, *Ann. Chem. Journ.* ii. 137.

trichloracetate on sodium aceto-acetic ether in presence of sodium ethylate.[1] In order to prepare it, one part of sodium is dissolved in ten parts of acetic ether and chloroform gradually added to the solution:



The product is boiled with caustic soda and the acid precipitated with hydrochloric acid. It is difficulty soluble in cold, more readily in hot water and crystallizes in thin needles, which soften and decompose at 290°. It gives a reddish violet colouration with ferric chloride and on heating with lime is resolved into carbon dioxide and metacresol.

Homohydroxyisophthalic acid (1 : 2 : 4 : 6) is formed when β-sulphoxylidic acid is heated to 220° with hydrochloric acid; it crystallizes from hot water in needles, which melt with decomposition at a few degrees above 270°. It gives no colouration with ferric chloride (Jacobsen).

Hydroxyxylidic acid (1 : 3 : 6 : 4) is obtained by fusing sulphamidoxylidic acid with caustic potash. It is also only very slightly soluble in hot water and crystallizes from dilute alcohol in microscopic prisms, which melt at 285°—290°, decomposing simultaneously into carbon dioxide and paracresol. It gives an intense dark red colouration with ferric chloride (Jacobsen).

MESITENYL COMPOUNDS.

2348 *Mesitenyl alcohol* or *mesityleneglycerol*, $C_6H_3(CH_2.OH)_3$, is obtained by boiling its bromide with lead carbonate and water. It is a thick liquid, which readily dissolves in water and has a bitter taste.

Mesitenyl chloride, $C_6H_3(CH_2Cl)_3$, is formed when the glycerol is heated with hydrochloric acid, as well as by the action of

[1] Oppenheim and Pfaff, *Ber. Deutsch. Chem. Ges.* vii. 929; viii. 884; Oppenheim and Precht, *ibid.* ix. 321.

chlorine on the vapour of mesitylene. It boils with decomposition at 277°—284°, but distils under diminished pressure without change.

Mesitenyl bromide, $C_6H_3(CH_2Br)_3$, is formed by the addition of the calculated quantity of bromine to boiling mesitylene and crystallizes from alcohol in long, microscopic needles, which melt at 94·5°.[1]

BENZENETRICARBOXYLIC ACIDS, $C_6H_3(CO_2H)_3$.

2349 *Trimesic acid* (1 : 3 : 5) was first obtained in small quantity by Fittig, together with a large amount of acetic acid, by boiling mesitylene with a solution of potassium dichromate in dilute sulphuric acid. A better yield is obtained by the oxidation of mesitylenic acid, the boiling being discontinued as soon as the latter has disappeared from the surface of the liquid.[2] It is formed in the same way from uvitic acid [3] and s-triethylbenzene,[4] and may also be obtained by heating hydromellitic acid with sulphuric acid:[5]

$$C_6H_6(CO_2H)_6 + 3SO_4H_2 = C_6H_3(CO_2H)_3 + 3CO_2 + 6H_2O + 3SO_2.$$

In addition to these methods it may be prepared by heating mellithic acid, $C_6(CO_2H)_6$, with glycerol,[6] and in smaller quantity when sodium metabromosulphobenzoate is fused with sodium formate.[7]

When propargylic acid, $CH \equiv C.CO_2H$, is exposed to sunlight, it is gradually converted into trimesic acid.[8] This polymerisation corresponds exactly to the formation of benzene from acetylene and to that of s-tribromobenzene from bromacetylene, which is also brought about by exposure to sunlight.[9]

Trimesic acid is somewhat soluble in cold, more readily

[1] Colson, *Compt. Rend.* xcvi. 71 ; xcvii. 177.
[2] *Ann. Chem. Pharm.* cxli. 142.
[3] Fittig and Furtenbach, *ibid.* cxlvii. 301 ; Baeyer, *Zeitschr. Chem.* 1868, 119.
[4] Jacobsen, *Ber. Deutsch. Chem. Ges.* vii. 1435 ; Friedel and Balsohn, *Bull. Soc. Chim.* xxxiv. 636.
[5] Baeyer, *Ann. Chem. Pharm. Suppl.* vii. 40 and 48.
[6] Baeyer, *Ann. Chem. Pharm*, clxvi. 340.
[7] Böttinger, *Ber. Deutsch. Chem. Ges.* vii. 1781.
[8] Baeyer, *ibid.* xix. 2185.
[9] Ssabanejew, *ibid.* xviii. Ref. 374.

in hot water, and crystallizes in hard, transparent, thick prisms, which melt above 300°, but sublime at lower temperature.

Normal sodium trimesate, $C_9H_3O_6Na_3$, forms an indistinct crystalline mass, which is very slightly soluble in water and almost absolutely insoluble in alcohol.

Acid sodium trimesate, $C_9H_5O_6Na$, is a very characteristic salt, crystallizing from hot water in splendid, lustrous plates, which are less soluble in cold water than the free acid.

Normal barium trimesate, $(C_9H_3O_6)_2Ba_3 + H_2O$, separates on the addition of barium chloride to the ammoniacal solution of the acid as a semi-solid mass, consisting of lustrous needles. It is scarcely soluble in cold, only very slightly in boiling water, from which it crystallizes, after standing for some time in the cold, in lustrous needles.

Acid barium trimesate, $(C_9H_5O_6)_2Ba + 4H_2O$, separates in hair-like, lustrous needles, when barium chloride is added to a hot aqueous solution of the acid.

Methyl trimesate, $C_9H_3O_6(CH_3)_3$, is readily formed by the action of methyl iodide on the silver salt, and forms small silky needles, melting at 143°.

Ethyl trimesate, $C_9H_3O_6(C_2H_5)_3$, crystallizes from alcohol in long, silky needles, which, according to Fittig and Furtenbach, melt at 129°, while Piutti gives the melting-point as 133°. The latter prepared this ether synthetically by the action of sodium on a mixture of ethyl formate and ethyl acetate while by replacing the former by the methyl ether or the latter by methyl acetate, he obtained a mixture of ethyl and methyl trimesate,[1] from which it follows that in the synthesis of the ethyl ether, the ethers of formylacetic acid, $CHO.CH_2.CO_2.C_2H_5$, and pyroracemic acid, $CH_3.CO.CO_2C_2H_5$, are simultaneously formed, three molecules then condensing to ethyl trimesate with elimination of water.

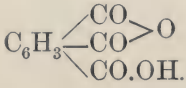
Sulphamidotrimesic acid, $C_6H_2(SO_2.NH_2)(CO_2H)_3$, is formed by the further oxidation of sulphamido-uvitic acid, and forms an acid potassium salt, $C_9H_6NSO_8K + H_2O$, which separates from hot water as a fibrous crystalline mass and is converted into acid potassium trimesate by heating to 210°—220° with concentrated hydrochloric acid. (Jacobsen.)

2350 *Trimellithic acid* (1 : 2 : 4) was first obtained by Baeyer, together with isophthalic acid and pyromellithic anhydride, by heating hydropyromellithic acid, $C_6H_6(CO_2H)_4$, with sulphuric

[1] *Ber. Deutsch. Chem. Ges.* xx. 537.

acid.[1] It is also formed by the oxidation of *a*-xylidic acid with potassium permanganate,[2] and by the fusion of the potassium salt of *a*-sulphophthalic acid with sodium formate.[3] It can also be obtained by means of the diazo-reaction from amidoterephthalic acid, the diazo-salt of which is converted into cyanoterephthalic acid by the action of a boiling solution of cuprous potassium cyanide, the trimellithic acid being prepared from this by boiling with caustic potash.[4] It is best obtained by the oxidation of colophony, which gives a yield of about 6 per cent. For this purpose, 100 grms. of the resin are boiled with two litres of a mixture of one volume of concentrated commercial nitric acid and two of water in a large retort for 6—8 hours, until all frothing has ceased; a fresh quantity of resin is then added and the process repeated, the alternate addition of colophony and nitric acid being continued until about one kilogr. of the former has been employed, the time occupied by this being about two weeks. The liquid is subsequently distilled until the residue commences to froth and is then poured into ten volumes of cold water, filtered after twenty-four hours and evaporated to a thin syrup, which deposits a mixture of isophthalic and trimellithic acids after standing for some days. This is filtered off, drained by a filter pump and separated by recrystallization from hot water.[5]

Trimellithic acid is tolerably soluble in water, from which it separates in warty crusts, which melt at 216° and simultaneously decompose into water and the anhydride, which solidifies on cooling to a crystalline mass, melting at 157°—158°, and has the following constitution:



Barium trimellithate, $(C_9H_3O_6)_2Ba_3 + 4H_2O$, forms warty crystals, which are not readily soluble in water.

Hemimellithic acid (1 : 2 : 3) is obtained, together with phthalic anhydride, by heating hydromellophanic acid, $C_6H_6(CO_2H)_4$, with sulphuric acid. It crystallizes in needles which are only slightly soluble in cold water, from which they are precipitated by

[1] *Ann. Chem. Pharm. Suppl.* vii. 40.
[2] Krinos, *Ber Deutsch. Chem. Ges.* x. 1494.
[3] Rée, *Inauguraldiss*, Bern 1886; *Ann. Chem. Pharm.* ccxxxiii. 230.
[4] Ahrens, *Ber. Deutsch. Chem. Ges.* xix. 1634.
[5] Schreder, *Ann. Chem. Pharm.* clxxii. 93.

hydrochloric acid. It decomposes on heating, with formation of phthalic anhydride and benzoic acid.

Barium hemimellithate, $(C_9H_3O_6)_2Ba_3 + 5H_2O$, crystallizes in short, compact needles.[1]

HYDROXYBENZENE-ALDEHYDO-DICARBOXYLIC ACIDS, $C_6H_2(OH)\begin{cases}CO.OH\\CHO\\CO.OH.\end{cases}$

2351 *Aldehydo-a-hydroxyisophthalic acid*, ($CO_2H : CO_2H : CHO : OH = 1 : 3 : 5 : 4$), is obtained, together with paraldehydosalicylic acid (Vol. III. Pt. IV. p. 491), by heating *a*-hydroxyisophthalic acid with caustic potash and chloroform. It crystallizes from hot water in matted needles, which melt at 260° with vigorous evolution of gas. It gives a blood-red colouration with ferric chloride. Its neutral solution is colourless, while its alkaline solution is yellow, and both show a green fluorescence.

Aldehydo-v-hydroxyisophthalic acid, (1 : 3 : 5 : 2), is prepared in a similar manner from v-hydroxyisophthalic acid, and crystallizes in fine, long needles, which melt with decomposition at 237°—238°. It gives a cherry-red colouration with ferric chloride, resembling that of v-hydroxyisophthalic acid, and its solutions show the same blue fluorescence. It dissolves in alkalis without any yellow colouration.[2]

HYDROXYBENZENETRICARBOXYLIC ACIDS, $C_6H_2(OH)(CO_2H)_3$.

2352 *Hydroxytrimesic acid* is formed by heating basic sodium salicylate or sodium phenate in a current of carbon dioxide to 360°, as well as by fusing sulphamidotrimesic acid with potash,[3] and by the oxidation of the two aldehydohydroxyisophthalic acids. It is slightly soluble in cold, more readily in hot water, and crystallizes from a concentrated solution in in-

[1] Baeyer, *Ann. Chem. Pharm. Suppl.* vii. 31; see also *ibid.* clxvi. 337.
[2] Reimer, *Ber. Deutsch. Chem. Ges.* xi. 793.
[3] Jacobsen, *Ann. Chem. Pharm.* ccvi. 167.

distinct prisms or needles, which contain one molecule of water and are united to crusts or warty masses, while it separates from dilute alcohol in fine, long, silky needles, containing two molecules of water. It gives a reddish brown colouration with ferric chloride. When it is heated above 100°, it decomposes into carbon dioxide, *a*-hydroxyisophthalic acid, salicylic acid and phenol.

Acid calcium hydroxytrimesate, $(C_9H_5O_7)_2Cu + 6H_2O$, is obtained by the addition of calcium chloride to a hot solution of the acid and separates on cooling in splendid, long needles.

Normal calcium hydroxytrimesate, $(C_9H_3O_7)_2Ca_3 + 8H_2O$, is a white precipitate, which is formed by the addition of calcium chloride to a solution of the acid neutralized by ammonia. It becomes anhydrous at 180° and then dissolves with tolerable readiness in cold water, but soon separates out, more rapidly on heating, in broad, hydrated needles.

Bariumhydroxytrimesate, $(C_9H_3O_7)_2Ba_3 + 8H_2O$, is a precipitate, which is almost insoluble in hot water.

Ethyl hydroxytrimesate, $C_9H_3O_7(C_2H_5)_3$, is very readily formed when hydrochloric acid is passed into a solution of the acid in absolute alcohol and crystallizes in prisms an inch in length, which melt at 84°. When alcoholic caustic soda is added to its alcoholic solution, the compound $C_6H_2(ONa)(CO_2.C_2H_5)_3$ separates out in small needles, which rapidly change into oblique prisms. These gradually dissolve when boiled with water, *sodium diethyl hydroxytrimesate*, $C_6H_2(OH)(CO_2.C_2H_5)_2CO_2Na + H_2O$, being deposited in hair-like needles on cooling. Free *diethyl hydroxytrimesic acid* may be prepared from this by means of hydrochloric acid, and crystallizes in broad needles, containing one molecule of water, which is lost at 100°; the anhydrous compound melts at 148° (Ost.)

Chlorotrimesic acid, $C_6H_2Cl(CO_2H)_3 + H_2O$. When hydroxytrimesic acid is distilled with phosphorus pentachloride, the chloride $C_6H_2Cl(COCl)_3$ is obtained as an oily liquid, which is converted into the acid by heating with water. This crystallizes from hot water in stellate groups of thick needles, or acute-angled tablets, melts at 278° and sublimes, a small amount of hydrochloric acid being simultaneously formed. It gives a yellowish brown precipitate with ferric chloride and is converted into trimesic acid by the action of sodium amalgam and water.

Barium chlorotrimesate, $(C_9H_2ClO_6)_2Ba_3 + 7H_2O$, is tolerably

soluble in cold water and is deposited on heating in matted needles, which redissolve as the solution cools.[1]

Hydroxytrimellithic acid, ($CO_2H : CO_2H : CO_2H : OH = 1 : 2 : 4 : 5$) is prepared by fusing sulphamidotrimellithic acid with caustic potash, and crystallizes from alcohol in transparent, compact prisms, but from hot water in smaller, lustrous prisms, containing two molecules of water, which they lose when heated, the anhydrous compound melting with decomposition at 240°—245°. It gives a deep brownish red colouration with ferric chloride and decomposes into carbon dioxide and meta-hydroxybenzoic acid when heated to 230°—240° with hydrochloric acid.[2]

PHLOROGLUCINOLTRICARBOXYLIC ACID, $C_6(OH)_3(CO_2H)_3$.

2353 The ethyl ether of this acid, which may also be termed *trihydroxytrimesic acid*, is formed when one atom of sodium is dissolved in two molecules of ethyl malonate and the mixture gradually heated to 145°.[3] The sodmalonic ether, which is the first product, probably decomposes into sodium ethylate and the residue $CO.CH.CO.OC_2H_5$, three of which then combine.

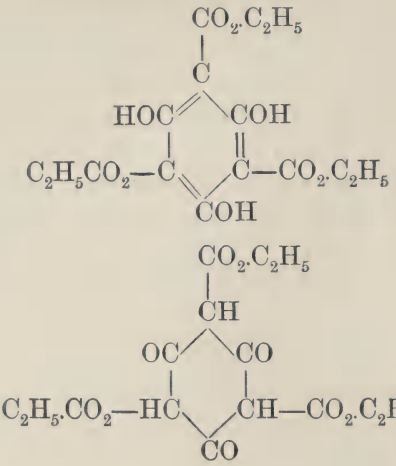
The same compound is formed when a mixture of ethyl malonate and zinc methyl is heated and the product, which probably has the composition $CH(ZnCH_3)(CO.OC_2H_5)_2$, warmed with hydrochloric acid, which decomposes it into zinc chloride, methane, alcohol and $CO.CH.CO.OC_2H_5$.[4]

Ethyl phloroglucinoltricarboxylate is only slightly soluble in alcohol and crystallizes in short, yellowish, lustrous needles, which melt at 104° and form a solution in ether which possesses a green fluorescence. On fusion with caustic potash it yields pure phloroglucinol.[5]

It shows a great similarity to succinylsuccinic ether and its constitution, like that of the latter and of phlorglucinol

[1] Ost, *Journ. prakt. Chem.* [2] xv. 308.
[2] *Ber. Deutsch. Chem. Ges.* xvi. 192.
[3] Baeyer, *ibid.* xviii. 3454.
[4] Lang, *ibid.* xix. 2937.
[5] This melts at 217°–218°; see also *ibid.* xix. 2186.

itself, can be expressed by two tautomeric formulæ (Pt. IV. p. 518).



THE METHYLETHYLBENZENES, $C_6H_4\begin{matrix}CH_3\\C_2H_5\end{matrix}$.

2354 *Paramethylethylbenzene*, or *Ethyltoluene*, is formed by the action of sodium on a mixture of parabromotoluene and ethyl bromide or iodide;[1] it is a liquid, which does not solidify in a freezing mixture and boils at 161°—162°. It is oxidized by dilute nitric acid to paratoluic acid. On bromination it yields bromo-ethyltoluene, which is converted into parabromotoluic acid on oxidation.[2] Fuming nitric acid converts it into two *dinitromethylethylbenzenes*, $C_6H_2(NO_2)_2CH_3(C_2H_5)$, one of which crystallizes in compact monosymmetric prisms or large tablets, melting at 52°, while the other does not solidify even in a freezing mixture. A mixture of nitric and sulphuric acids converts both into *trinitromethylethylbenzene*, $C_6H(NO_2)_3CH_3(C_2H_5)$, which crystallizes from boiling alcohol in stellate groups of short, hard prisms, melting at 92°.

Metamethylethylbenzene has been prepared from metabromotoluene and ethylbromide,[3] and is also formed, together with

[1] Fittig and Glinzer, *Ann. Chem. Pharm.* cxxxvi. 312; Jannasch and Dieckmann, *Ber. Deutsch. Chem. Ges.* vii. 1513.
[2] Mörse and Remsen, *Ber. Deutsch. Chem. Ges.* xi. 224.
[3] Wroblewsky, *Ann. Chem. Pharm.* cxcii. 196.

toluene and other hydrocarbons, when abietic acid, the chief constituent of pine resin, is distilled with zinc dust.[1] It is a liquid, which boils at 158°—159°, and is oxidized to isophthalic acid by chromic acid solution.

Orthomethylethylbenzene is formed by the action of sodium on a mixture of orthobromotoluene and ethyl bromide and is a liquid, which boils at 160° and is oxidized to orthotoluic acid by nitric acid.[2] This is also formed, together with phthalic acid, when the hydrocarbon is oxidized in the cold with potassium permanganate, but the chief product is terephthalic acid, which is not formed at a higher temperature, since complete combustion then takes place.[3] This remarkable formation of terephthalic acid is probably analogous to that of benzoic acid by the oxidation of benzene (Pt. III. p. 76). When the hydrocarbon is brominated in the cold, *bromorthomethylethylbenzene*, $C_6H_3Br(CH_3)C_2H_5$, is formed as a liquid, boiling at 220°—221°.

Amidomethylethylbenzene, $C_6H_3(NH_2)(CH_3)C_2H_5$, is formed by heating orthotoluidine with ethyl alcohol and zinc chloride to 260°—280°. It is an oily liquid, which has an aromatic odour, boils at 229°—230° and gives the carbamine reaction. It is not known from which of the methylethylbenzenes it is derived.[4]

TOLYLMETHYLKETONES, $C_6H_4\begin{matrix}CH_3\\CO.CH_3\end{matrix}$.

2355 *Paratolylmethylketone* was first prepared by Michaelis, who heated toluene with acetic anhydride and a little aluminium chloride.[5] A better yield is obtained when aluminium chloride is suspended in carbon disulphide and a mixture of acetyl chloride and toluene gradually added at the ordinary temperature with constant agitation.[6]

It is also formed, accompanied by smaller quantities of nitro-products, by the action of nitric acid on cymene, $CH_3.C_6H_4.C_3H_7$,[7] and is a liquid, which has a pleasant odour, melts at 220° and is oxidized to paratoluic acid by dilute nitric acid and to terephthalic acid by potassium permanganate.

[1] Ciamician, *Ber. Deutsch. Chem. Ges.* xi. 269.
[2] Claus and Mann, *ibid.* xviii. 1121.
[3] Claus and Pieszcek, *ibid.* xix. 3083.
[4] Benz, *ibid.* xv. 1646.
[5] *Ibid.* xv. 185.
[6] Claus and Riedel, *ibid.* xix. 234.
[7] Bladin and Widman, *ibid.* xix. 584.

Methyltolylacetoxime, $CH_3.C_6H_4.C(NOH)CH_3$, is scarcely soluble in water, readily in alcohol and separates from hot petroleum-ether in short, lustrous crystals, melting at 88°.

Methyltolylketonephenylhydrazine, $CH_3.C_6H_4.C(N_2H.C_6H_5)CH_3$ crystallizes from alcohol in lustrous prisms, melting at 97°, which rapidly change in the air into a brown liquid (Bladin and Widmann).

Metatolylmethylketone is formed, according to Essner and Gossin, when acetyl chloride and aluminium chloride are gradually added to a mixture of toluene with a little aluminium chloride. It is a liquid, which has an aromatic odour, boils at 224°—225° and is converted by oxidation with potassium permanganate into isophthalic acid. On heating with alcoholic potash, it decomposes into acetic acid and toluene. Its isomerides are also present in the crude product, since small quantities of phthalic and terephthalic acids are formed when this is oxidized.[1]

ETHYLBENZENECARBOXYLIC ACIDS OR ETHYLPHENYLFORMIC ACIDS,

$$C_6H_4\begin{cases}C_2H_5\\CO_2H\end{cases}.$$

2356 *Para-ethylbenzenecarboxylic acid* is formed by the oxidation of paradiethylbenzene with nitric acid,[2] and by the action of sodium and carbon dioxide on parabromethylbenzene.[3] It crystallizes from hot water in lustrous plates and from alcohol in small prisms, which melt at 110°—111°, sublime at a lower temperature and are converted into terephthalic acid by oxidation.

Ortho-ethylbenzenecarboxylic acid is obtained when orthoacetylbenzenecarboxylic acid, $CH_3.CO.C_6H_4.CO_2H$, is heated to 180° with amorphous phosphorus and hydriodic acid, and may be prepared in a similar manner from phthalylacetic acid:

$$C_6H_4\begin{cases}CO\\CO\end{cases}CH.CO_2H + 4H = C_6H_4\begin{cases}CH_2.CH_3\\CO.OH\end{cases} + CO_2.$$

[1] *Bull. Soc. Chim.* xlii. 95.
[2] Fittig and König, *Ann. Chem. Pharm.* cxliv. 290.
[3] Kekulé and Thorpe, *Ber. Deutsch. Chem. Ges.* ii. 421.

When water is added to its hot alcoholic solution, it is precipitated in oily drops, which rapidly solidify to scales or plates resembling those of benzoic acid, while it crystallizes from hot water in flat, lustrous needles, melting at 68°.[1]

Ethylhydroxybenzenecarboxylic acid, $C_6H_3(OH)(C_2H_5)CO_2H$, was obtained by Beilstein and Kuhlberg by the action of carbon dioxide and sodium on *a*-ethylphenol (p. 4). It melts at 118°—120°, and gives a violet colouration with ferric chloride.[2]

METHYLPHENYLACETIC ACIDS, $C_6H_4\begin{matrix}CH_3\\CH_2.CO_2H\end{matrix}$.

Paramethylphenylacetic acid was obtained by Cannizzaro from paraxylyl chloride, by heating this with potassium cyanide and decomposing the nitril with caustic potash; he did not however publish any account of its properties.[3] Radziszewski and Wispek then prepared it from paraxylyl bromide.[4] It is also formed when paratoluylcarboxylic acid is treated with hot water, iodine and red phosphorus and crystallizes in lustrous plates or needles, melting at 89°.

Metamethylphenylacetic acid was prepared by Vollrath, who named it *a*-xylic acid, from the crude chloride of coal-tar xylene.[5] Radziszewski and Wispek then obtained it from pure metaxylyl bromide. It crystallizes from hot water in broad, satin lustrous needles, melting at 53°—54°.

Orthomethylphenylacetic acid was also prepared by these chemists; it forms long, silky needles, melting at 86°.

METHYLSTYROLENE OR TOLYLETHYLENE, $CH_3.C_6H_4.CH=CH_2$.

2357 This hydrocarbon is formed when metamethylcinnamic acid, $CH_3.C_6H_4.CH=CH.CO_2H$, is allowed to stand in contact with concentrated hydrobromic acid at the ordinary temperature, the product being then treated with water and sodium carbonate.

[1] Gabriel and Michael, *Ber. Deutsch. Chem. Ges.* x. 2206; Zincke and Fröhlich, *ibid.* xx. 1056.
[2] *Ann. Chem. Pharm.* clvi. 213.
[3] *Ibid.* cxxiv. 252.
[4] *Ber. Deutsch. Chem. Ges.* xv. 1743.
[5] *Zeitschr. Chem.* 1868, 489.

It is a liquid, which boils at 164° and, like styrolene, changes into a polymeric modification when preserved.

Methylstyrolene bromide, $CH_3.C_6H_4.CHBr.CH_2Br$, forms crystals, melting at 45°. On boiling with alcoholic potash it is converted into *methyl-β-bromostyrolene*, $CH_3.C_6H_4.CBr=CH_2$, a liquid which has an unpleasant odour and decomposes when heated. The isomeric *methyl-α-bromostyrolene*, $CH_3.C_6H_4.CH=CHBr$, is formed by the action of bromine on an aqueous solution of sodium methylcinnamate as an oily, pleasant smelling liquid, which boils at 242°.[1]

METHYLPHENYL-HYDROXYACETIC ACIDS, $C_6H_4\begin{cases}CH_3\\CH(OH).COOH\end{cases}$.

Metamethylmandelic acid. The nitril of this acid is formed when hydrochloric acid is added to an ethereal solution of metatolualdehyde in which powdered potassium cyanide is suspended. It is an oily liquid, which is converted into the acid by heating to 60°—70° with fuming hydrochloric acid; this is readily soluble in water and alcohol and crystallizes from benzene in lustrous plates, melting at 84°.[2]

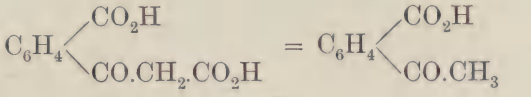
Paramethylmandelic acid is formed by the action of water and sodium amalgam on paratoluylcarboxylic acid and crystallizes from hot water in large tablets, melting at 145°—146°.[3]

KETONIC ACIDS, $C_9H_8O_3$.

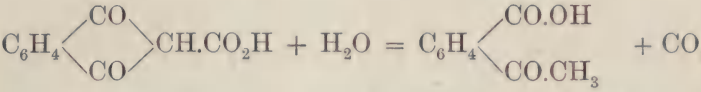
2358 *Para-acetylbenzoic acid*, $C_6H_4(CO.CH_3)CO_2H$, is formed together with terephthalic acid, when hydroxyisopropylbenzoic acid, $(CH_3)_2C(OH)C_6H_4.CO_2H$, is oxidized with chromic acid solution. It is only very slightly soluble in boiling water and crystallizes in lustrous needles, which melt at 200° and sublime at a higher temperature.[4]

[1] Müller, *Ber. Deutsch. Chem. Ges.* xx. 1212.
[2] Bornemann, *ibid.*
[3] Claus and Kroseberg, *ibid.* xx. 2048.
[4] R. Meyer, *ibid.* xii. 1071; *Ann. Chem. Pharm.* ccxix. 259.

Ortho-acetylbenzoic acid or *Acetophenonecarboxylic acid.* When phthalic anhydride is heated with acetic anhydride and sodium acetate, phthalylacetic acid is formed and is converted by alkalis into benzoylacetocarboxylic acid. This decomposes on boiling with water into carbon dioxide and ortho-acetylbenzoic acid :

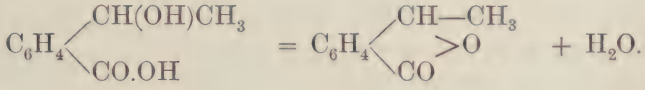


It is also formed when phthalylacetic acid is heated to 200° with water :



It is deposited, when its solution in hot water is allowed to cool, in fine globules, which solidify to groups of crystals possessing a vitreous lustre, which melt at 114°—115° and have a sweet taste.[1]

When sodium amalgam is added to its alkaline solution, it is converted into *hydro-acetophenonecarboxylic acid,* which, however immediately decomposes into *a-methylphthalide* and water when it is liberated by hydrochloric acid (Supt. IV. p. 442) :



The latter substance is an oily liquid, which solidifies below 0° and boils at 275°—276.°[2]

Orthotrichloracetylbenzoic acid, $C_6H_4(CO.CCl_3)CO_2H$, is formed when the acid is suspended in warm acetic acid and treated with chlorine. It crystallizes from a large quantity of hot water in long needles, melting at 144°, and is decomposed by alkalis into chloroform and phthalic acid.

Orthotribromacetylbenzoic acid, $C_6H_4(CO.CBr_3)CO_2H$, is obtained in a similar manner to the chlorine compound and also forms long needles, melting at 159·5°—160°, which undergo a similar decomposition with alkalis.

Paratoluylcarboxylic acid, $CH_3.C_6H_4.CO.CO_2H$, is formed by

[1] Gabriel and Michael, *Ber. Deutsch. Chem. Ges.* x. 1551.
[2] Gabriel, *ibid.* xx. 2500.

the action of aluminium chloride on a mixture of toluene and amyloxalyl chloride:

$$C_6H_5.CH_3 + COCl.CO.OC_5H_{11} = C_6H_4\begin{matrix}CH_3\\CO.CO.OC_5H_{11}\end{matrix} + HCl.$$

The product is decomposed with alcoholic potash and the acid liberated by hydrochloric acid.[1] It is also formed by the oxidation of paratolylmethylketone with an alkaline solution of potassium ferricyanide.[2] It crystallizes from petroleum-ether in large flat needles, which decompose on preservation after a few days, are readily soluble in water, soften at 80° and become completely liquid at 99°. It is oxidized to paratoluic acid by potassium permanganate. If it be dissolved in sulphuric acid and treated with benzene which contains thiophene, the liquid becomes deep red, changing to blue-violet, and on the addition of water and evaporation of the benzene deposits the indophenin (p. 68), which has been formed, as a red powder, which is readily soluble in alcohol and dyes silk pink.

HOMOPHTHALIC ACIDS, $C_6H_4\begin{matrix}CO_2H\\CH_2.CO_2H\end{matrix}$.

2359 *Homo-orthophthalic acid.* Hlasiwetz and Barth obtained *isuvitic acid*[3] by fusing the resin contained in gamboge with caustic potash, and W. Wislicenus found that benzylcyanide-orthocarboxylic acid is formed when phthalide is heated with potassium cyanide:[4]

$$C_6H_4\begin{matrix}CH_2\\CO\end{matrix}\!\!>O + KCN = C_6H_2\begin{matrix}CH_2.CN\\CO.OK\end{matrix}.$$

It separates from a hot solution in acetic acid as a yellowish sandy power, which after purification becomes white and indistinctly crystalline, and is converted by boiling with caustic potash into *phenylacetorthocarboxylic acid* or homo-orthophthalic acid, which has been shown by Schuder to be identical

[1] Roser, *Ber. Deutsch. Chem. Ges.* xiv. 1750.
[2] Buchka and Irisch, *ibid.* xx. 1762.
[3] *Ann. Chem. Pharm.* cxxxviii. 68.
[4] *Ber. Deutsch. Chem. Ges.* xviii. 172; *Ann. Chem. Pharm.* ccxxxiii, 101.

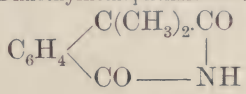
with isuvitic acid.[1] It crystallizes from water in short, rhombic prisms, which form saw-shaped aggregates and melt at 175°. On heating with soda-lime it yields toluene and on fusion with caustic potash is resolved into carbon dioxide and orthotoluic acid. If it be heated with acetyl chloride, *homophthalic anhydride*, $C_9H_6O_3$, is formed and crystallizes from benzene in long, pliant prisms, melting at 141°.

Homophthalimide, $C_6H_4\left\langle\begin{matrix}CH_2—CO\\CO—NH\end{matrix}\right\rangle$, is obtained by heating ammonium phthalate; the distillate forms a crystalline mass covered with long crystals and crystallizes from glacial acetic acid in short needles, melting at 233°.[2] It dissolves in alcohol forming a solution which has a green fluorescence; on heating with caustic potash, methyl alcohol and methyl iodide, *dimethylhomophthalimide*, $C_9H_5(CH_3)_2NO_2$, is formed, and crystallizes from hot water in flat needles, melting at 119°—120°. On further heating with caustic potash and methyl iodide, *trimethylhomophthalimide* $C_9H_4(CH_3)_3NO_2$, is obtained, and forms long needles, which melt at 102°—103° and are insoluble in alkalis.

Homophthalmethylimide, $C_6H_4\left\langle\begin{matrix}CH_2—CO\\CO—NCH_3\end{matrix}\right\rangle$, is formed by heating the methylamine salt of homophthalic acid and distils at 314°—318°. It crystallizes from boiling water in long needles, melting at 123°, and is converted into trimethylhomophthalimide by heating with caustic potash and methyl iodide.

When this substance is heated to 230°—240° with fuming hydrochloric acid, methylamine is eliminated and the anhydride of a dibasic acid formed, which is also formed from dimethylhomophthalimide with elimination of ammonia, and crystallizes from alcohol in flat needles, melting at 82·5°—83°. In this compound and also in dimethylphthalimide, the two methyl groups are combined with one carbon atom, the constitution of the two bodies being represented by the following formulæ:[3]

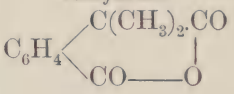
Dimethylhomophthalimide.



$$C_6H_4\left\langle\begin{matrix}C(CH_3)_2.CO\\ \quad\quad\quad\quad |\\ CO——NH\end{matrix}\right.$$

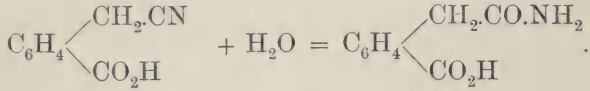
Anhydride.

$$C_6H_4\left\langle\begin{matrix}C(CH_3)_2.CO\\ \quad\quad\quad\quad |\\ CO——O\end{matrix}\right.$$



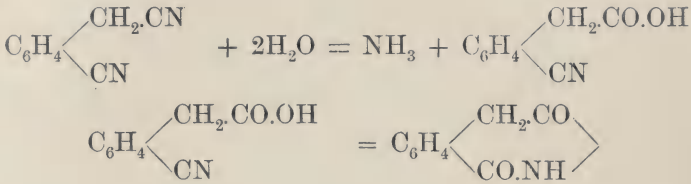
[1] *Monatsh. Chem.* vi. 168.
[2] Gabriel, *Ber. Deutsch. Chem. Ges.* xix. 1653.
[3] *Ibid.* ii. 2363; xx. 1198.

Homo-orthophthalamic acid is formed when benzylcyanide-orthocarboxylic acid is heated with concentrated sulphuric acid and the solution poured into water :



It crystallizes in needles, which melt at 185°—187° and on further heating are converted into orthohomophthalimide, while acid ammonium homo-orthophthalate is formed when it is boiled with water.[1]

Homo-orthophthalonitril, $C_6H_4(CN)CH_2.CN$. When ortho-tolunitril is heated almost to the boiling point and treated with chlorine, *orthocyanobenzyl chloride*, $C_6H_4(CN)CH_2Cl$, is obtained. This substance forms crystals, melting at 60°—61·5° and is converted by heating with potassium cyanide and dilute alcohol into the nitril, which crystallizes in small, colourless flakes, melting at 81°. If it be heated with sulphuric acid and the solution poured into water, homophthalimide separates out. Cyanophenylacetic acid is probably first formed in this reaction and then undergoes an intermolecular change.[2]

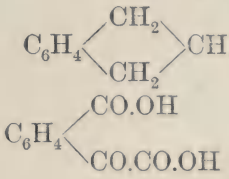


Homoterephthalic acid has been prepared by the oxidation of propylisopropylbenzene with dilute nitric acid ; it is a powder, which is insoluble in almost all solvents and sublimes when heated without melting.[3]

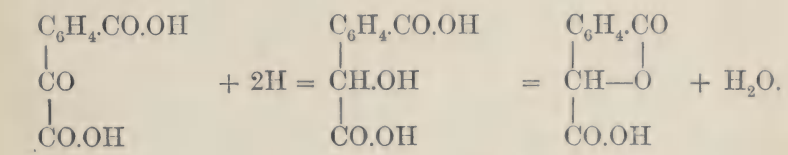
[1] *Ber. Deutsch. Chem. Ges.* xx. 1203.
[2] Gabriel and Otto, *ibid.* xx. 2222 ; Gabriel, *ibid*, xx. 2499.
[3] Paternò and Spica, *ibid.* x. 1746.

PHTHALIDECARBOXYLIC ACID, $C_9H_6O_4$.

The product of the action of orthoxylylene bromide on sodmalonic ether or sodaceto-acetic ether is hydrindonaphthenecarboxylic acid, and this is oxidized in alkaline solution by potassium permanganate in the following way:



The dibasic acid, which is thus formed, decomposes on heating with formation of phthalic acid and phthalic anhydride, while it is reduced to phthalidecarboxylic acid by the action of sodium amalgam on its aqueous solution:



It crystallizes from hot water in lustrous flakes, melting at 149·5°, and decomposes at 180° into carbon dioxide and phthalide.[1]

THE PROPYLBENZENES.

2360 *Isopropylbenzene or Cumene*, $C_6H_5.CH(CH_3)_2$. Gerhardt and Cahours found that the *cuminol*, $C_{10}H_{12}O$, which is contained in Roman cumin oil (*Cuminum cyminum*) together with *cymene* (*cyméne*), is the aldehyde of *cumic acid*, $C_{10}H_{12}O_2$, which decomposes on heating with baryta into carbon dioxide and cumene (*cumène*).[2] The latter is oxidized to benzoic acid by dilute nitric acid,[3] and was subsequently considered to be propylbenzene. This was prepared synthetically by Fittig, Schäffer and

[1] Scherks, *Ber. Deutsch. Chem. Ges.* xviii. 378.
[2] *Ann. Chem. Pharm.* xxxviii. 88.
[3] Abel, *ibid.* lxiii. 308.

König, by the replacement of an atom of hydrogen in benzene by primary propyl; the hydrocarbon thus obtained, however, proved not to be identical with cumene and these chemists therefore looked upon the latter as isopropylbenzene.[1] This view was confirmed by Jacobsen, who prepared cumene by the action of sodium on a mixture of bromobenzene, isopropyl iodide and ether.[2] It may also be obtained by the action of aluminium bromide on a mixture of benzene and isopropyl bromide or normal propyl bromide,[3] since Kekule and Schrötter have shown that the latter is converted into isopropyl bromide by heating with aluminium bromide;[4] the chlorides may be employed in these reactions instead of the bromides.[5] Liebermann obtained cumene by heating benzidene chloride, $C_6H_5.CHCl_2$, with zinc methyl:[6]

$$C_6H_5.CHCl_2 + Zn(CH_3)_2 = C_6H_5.CH\begin{matrix}CH_3\\CH_3\end{matrix} + ZnCl_2.$$

It is a liquid which boils at 153° and has a specific gravity of 0·880 at 0°. On treatment with bromine and a little aluminium, it decomposes with formation of hexbromobenzene, isopropyl bromide and their substitution products (Gustavson).

Parabromocumene, $C_6H_4Br.CH(CH_3)_2$, is formed when bromine is gradually added to well-cooled cumene, in which a little iodine has been dissolved. It is a liquid, boils at 216°—217·5°, and is converted into parabromobenzoic acid by oxidation with potassium permanganate.[7]

Orthobromocumene is formed by the action of phosphorus pentabromide on orthocumenol, and is a liquid, boiling at 205°—207°,[8] which is however probably a mixture of the isomeric bromocumenes.

Pentabromocumene, $C_9H_7Br_5$, is formed when a mixture of cumene and an excess of bromine is allowed to stand for a few weeks. It crystallizes from alcohol in stellate groups of needles, which have a magnificent lustre, melt at 97° and are decomposed by boiling alcoholic potash with loss of bromine, it being thus proved that a portion of the bromine is contained in the alcohol radical.[9]

[1] *Ann. Chem. Pharm.* cxlix. 324.
[2] *Ber. Deutsch. Chem. Ges.* viii. 1260.
[3] Gustavson, *ibid.* xi. 1251.
[4] *Ibid.* xii. 2279.
[5] Silva, *Bull. Soc.* xliii. 317.
[6] *Ber. Deutsch. Chem. Ges.* xiii. 45.
[7] Jacobsen, *ibid.* xii. 429.
[8] Fileti, *Gaz. Chim.* xvi. 113.; *Ber. Deutch. Chem. Ges.* xix. Ref 553.
[9] Meusel, *Zeitschr. Chem.* 1867, 322; Fittig, Schäffer and König, *Ann. Chem. Pharm.* cxlix. 326.

Para-iodo-cumene, $C_6H_4I.CH(CH_3)_2$, has been prepared from paramidocumene, and is a liquid, which has an aromatic odour, boils at 234° and yields para-iodobenzoic acid on oxidation.[1]

Cumeneparasulphonic acid, $C_6H_4(C_3H_7)SO_3H$, was first prepared by Gerhardt and Cahours, who dissolved cumene in fuming sulphuric acid, and was subsequently investigated by Jacobsen [2] and Fittig, Schäffer and König.[3] It crystallizes in anhydrous, nacreous scales, which are very deliquescent. The following are its most characteristic salts:

Barium cumeneparasulphonate, $(C_9H_{11}SO_3)_2Ba + H_2O$, crystallizes from hot water in nacreous plates, which readily lose their water of crystallization on heating. One hundred parts of the solution saturated at 16° contain 4·4 parts of the anhydrous salt (Claus and Tonn).

Strontium cumeneparasulphonate, $(C_9H_{11}SO_3)_2Sr+2H_2O$, forms stellate groups of needles, which dissolve in an equal weight of cold water. When the saturated solution is heated to 100°, it solidifies to a crystalline mass, consisting of the anhydrous salt, which re-dissolves on cooling.

Cumeneparasulphamide, $C_6H_4(C_3H_7)SO_2.NH_2$, forms crystals, which melt at 112° (Claus and Tonn). Potassium permanganate oxidizes it to a sulphamic acid, which is converted into para-hydroxybenzoic acid on fusion with caustic potash (Spica).

Hydroxyisopropylbenzenesulphonic acid, $C_6H_4(SO_3H)C(OH)(CH_3)_2$, is formed by the oxidation of cumeneparasulphonic acid with potassium permanganate. It forms a potassium salt, which is readily soluble in alcohol and is converted by treatment with phosphorus chloride and then ammonia into *propenylbenzenesulphamide*, $C_6H_4(SO_2.NH_2)C_3H_5$, which melts at 152°.[4]

Cumene-orthosulphonic acid is formed, according to Spica, in small quantity in the preparation of the para-acid,[5] and is the chief product when cumene is sulphonated at 100°, or when a solution of cumene in fuming sulphuric acid is allowed to stand for several weeks.[6] It is extremely soluble in water and crystallizes in small, very deliquescent needles. It is converted into orthocumic acid when its salts are fused with sodium formate.

[1] Louis, *Ber. Deutsch. Chem. Ges* xvi. 105.
[2] *Ann. Chem. Pharm.* cxlvi. 86.
[3] *Ibid.* cxlix. 329.
[4] Meyer and Baur, *Ber. Deutsch. Chem. Ges.* xii. 2239.
[5] *Ibid.* xii. 2367.
[6] Claus, Woge and Tonn, *ibid.* xviii. 1239.

Barium cumene-orthosulphonate, $2(C_9H_{11}SO_3)_2Ba+7H_2O$, crystallizes in warty masses composed of needles; 100 parts of the solution saturated at 16° contain 16·5 parts of anhydrous salt.

Cumene-orthosulphamide crystallizes in lustrous needles, melting at 127°. Potassium permanganate oxidizes it to a sulphamic acid, which is converted into salicylic acid by fusion with caustic potash.

The cumenesulphonic acids yield the cumophenols on fusion with caustic potash.[1]

Paracumophenol, $C_6H_4(OH)CH(CH_3)_2$, crystallizes in needles, melts at 61° and boils at 228°—229°.

Paracumophenyl methyl ether, $C_6H_4(OCH_3)CH(CH_3)_2$, is a liquid, which smells like aniseed and boils at 212°—213°.

Paracumophenyl ethyl ether, $C_6H_4(OC_2H_5)CH(CH_3)_2$, boils at 220° and yields ethylparahydroxybenzoic acid on oxidation.

Orthocumophenol is a liquid, which boils at 218·5°, does not solidify in a freezing mixture and gives a violet colouration with ferric chloride. Its ethyl ether boils at 213° and yields an oily liquid on oxidation, which is probably ethylsalicylic acid.

Fileti obtained a cumophenol from cumidine, which boils at 212°—212·5° and which he considers as the ortho-compound.[2] This substance is obviously a mixture, since cumidine itself is a mixture of several isomerides.

Metacumophenol was prepared by Jacobsen by heating isohydroxycumic acid, $C_6H_5(OH)CH(CH_3)_2CO_2H$, to 190° with hydrochloric acid. It boils at 228° and solidifies on cooling to a fibrous, crystalline mass, melting at 26°. Its aqueous solution is coloured a faint blue by ferric chloride, which produces a green colouration in an alcoholic solution.[3]

Nitrocumene, $C_6H_4(NO_2)CH(CH_3)_2$, is formed as an oily liquid when cumene is dissolved in fuming nitric acid and the solution precipitated with water (Nicholson).[4]

According to Posspechow, one part of cumene is gradually added to 2·5 parts of nitric acid of sp. gr. 1·52, which is well cooled with ice, and the product purified by distillation with water. It decomposes on boiling, solidifies in solid carbon dioxide and melts at —35°.[5]

[1] Paternò and Spica, *Gaz. Chim. ital.* vi. 535; Spica, *ibid.* viii. 406; ix. 433.
[2] *Ibid.* xvi. 113; *Ber. Deutsch. Chem. Ges.* xix. 551.
[3] *Ibid.* xi. 1062; see also Widmann, *ibid.* xix. 251.
[4] *Ann. Chem. Pharm.* lxv. 58.
[5] *Ber. Deutsch. Chem. Ges.* xix. Ref. 169.

Trinitrocumene, $C_6H_2(NO_2)_3CH(CH_3)_2$, is formed by heating cumene with a mixture of nitric and sulphuric acids, and crystallizes from hot alcohol in long, lustrous needles, melting at 109° (Fittig, Schäffer and König).

Amidocumene or *Cumidine*, $C_6H_4(NH_2)_2CH(CH_3)_2$, was prepared by Nicholson from nitrocumene by reduction with ammonium sulphide. It is an oily liquid, which rapidly becomes yellow and finally dark-brown in the air and has a characteristic odour and a burning taste. It solidifies in a freezing mixture to quadratic tablets, which rapidly melt when the temperature is allowed to rise. One specimen was observed to solidify at the winter temperature and remained solid throughout the summer. It boils at 225°, colours pine-wood yellow, in the same way as aniline, and forms salts, which crystallize well.

Nitrocumidine, $C_6H_3(NO_2)(NH_2)CH(CH_3)_2$, was obtained by Cahours by the reduction of the product obtained by the action of a mixture of nitric and sulphuric acids on cumene, which he considered to be dinitrocumene; but which is the trinitro-compound and, like trinitropseudocumene, loses ammonia on reduction. Nitrocumidine crystallizes in yellowish scales, melting at 100°, and forms salts, which crystallize well.[1]

Nitrocumene and the products obtained from it are obviously mixtures of isomeric compounds, the existence of which was unsuspected at the period of their preparation.

Paramidocumene, $C_6H_4(NH_2)CH(CH_3)_2$, is formed when equal molecules of zinc chloride, aniline and isopropylalcohol are heated to 260°. It is a liquid, which has an aromatic odour, becomes brown in the air and boils at 216°—218°.[2]

2361 *Propylbenzene*, $C_6H_5.C_3H_7$, was first prepared by Fittig, Schäffer and König by the action of sodium on a mixture of bromobenzene and propyl iodide,[3] and was subsequently obtained by Paternò and Spica by the gradual addition of zinc ethyl to benzyl chloride.[4] It is also formed, together with other products, when a mixture of benzene and aluminium chloride is acted on by allyl chloride in the cold,[5] while diphenylpropane and a little isopropylbenzene are formed if the mixture be heated.[6] It is a liquid, which has a pleasant smell, boils at 157°, has a sp. gr. of 0·881 at 0° and only yields liquid

[1] *Jahresb. Chem.* 1847–1848, 665.
[2] Louis, *loc. cit.*
[3] *Ann. Chem. Pharm.* cxlix. 324.
[4] *Gaz. Chim. ital.* vii. 21.
[5] Wispek and Zuber, *Ann. Chem. Pharm.* ccxviii. 374.
[6] Silva, *Bull. Soc. Chim.* xliii. 317 and 588.

substitution products when acted on by a mixture of nitric and sulphuric acids.

Parabromopropylbenzene, $C_6H_4Br.C_3H_7$, is formed when the hydrocarbon is treated with bromine in presence of iodine; it is a liquid, which boils at 220° and is oxidized to parabromobenzoic acid by nitric acid.[1] The same compound is also formed, accompanied by *orthobromopropylbenzene*, when bromine is allowed to act upon the hydrocarbon in the dark; the liquid thus prepared has a persistent, pleasant odour, boils at 221°—223° and yields a mixture of para- and ortho-bromobenzoic acids on oxidation with potassium permanganate.[2]

When propylbenzene is treated with bromine in the sunlight, a monobromide is first formed, which probably has the constitution $C_6H_5.CHBr.CH_2.CH_3$. The dibromide, $C_6H_5.CBr_2.CH_2.CH_3$, is formed by the further action of bromine, while the compound, $C_6H_5.CHBr.CHBr.CH_3$, which will be subsequently described, is formed if the action be carried on in a hot solution in the dark (Schramm).

Fittig, Schäffer and König obtained a viscid mass, consisting chiefly of *tetrabromopropylbenzene*, $C_9H_8Br_4$, by the action of an excess of bromine on propylbenzene.

Para-iodopropylbenzene, $C_6H_4I.C_3H_7$, was prepared by Louis from paramidopropylbenzene as a liquid which has an aromatic odour, boils at 250° and is converted into para-iodobenzoic acid by oxidation.

Propylbenzenesulphonic acid, $C_6H_4(C_3H_7)SO_3H$, is formed in two isomeric modifications, when propylbenzene is dissolved in slightly fuming sulphuric acid. These compounds can be separated by means of their barium salts.

Barium propylbenzeneparasulphonate, $(C_9H_{11}SO_3)_2Ba$, crystallizes in anhydrous plates.

Barium propylbenzeneorthosulphonate, $(C_9H_{11}SO_3)_2Ba + 2H_2O$, is more readily soluble in water and crystallizes in fascicular groups of microscopic needles.

When these two salts are converted into the corresponding potassium salts and the latter fused with caustic potash, the propylphenols are obtained.[3]

Parapropylphenol, $C_6H_4(C_3H_7)OH$, has also been prepared from paramidopropylbenzene[4] and forms an oily liquid, which

[1] R. Meyer, *Journ. Prakt. Chem.*, [2] xxxiv. 101.
[2] Schramm, *Ber. Deutsch. Chem. Ges.* xviii. 1274.
[3] Spica, *Gaz. Chim. Ital.* viii. 406.
[4] Louis, *Ber. Deutsch. Chem. Ges.* xvi. 105.

has an aromatic odour, boils at 230°—232° and does not solidify in a freezing mixture. Its aqueous solution gives a faint violet colouration with ferric chloride, which changes to green on standing.

Parapropylphenyl methyl ether, $C_6H_4(C_3H_7)OCH_3$, is a liquid, which has an odour resembling that of aniseed, boils at 214°—215·5° and is oxidized by chromic acid to anisic acid.

Orthopropylphenol boils at 224·6°—226·6° and forms a methyl ether, which boils at 207°—209.

Propylpyrogallol, $C_6H_2(OH)_3C_3H_7$. The dimethyl ether of this substance occurs in the fraction of creosote which boils at 285° (Part IV. p. 37), and decomposes, when heated with concentrated hydrochloric acid to 130°, into methyl chloride and propylpyrogallol, which crystallizes from benzene in prisms, melting at 79°—80°, and is extremely soluble in water and alcohol.

Propylpyrogallol dimethyl ether, $C_6H_2(OCH_3)(OH)C_3H_7$, is an oily liquid, which boils at 285° and is converted by acetic anhydride into the acetyl-derivative, $C_6H_2(OCH_3)(OC_2H_3O)C_3H_7$, which crystallizes in white prisms and melts at 87°. It is converted by bromine into the compound $C_6Br_2(OCH_3)(OH)C_3H_7$, which forms crystals, melting at 108°—109°, and yields the dimethyl ether of dihydroxyquinone (Part III. p. 156) on oxidation.[1]

Paramidopropylbenzene, $C_6H_4(NH_2)C_3H_7$, was obtained by Louis by heating aniline with propyl alcohol and zinc chloride to 260°, as a liquid which has an aromatic odour, boils at 224°—226° and becomes brown in the light.

THE PHENYLPROPYL ALCOHOLS.

2362 *Primary phenylpropylalcohol*, $C_6H_5.C_3H_6.OH$. The cinnamic ether of this occurs, together with that of cinnyl or phenylallyl alcohol, $C_6H_5.CH{=}CH.CH_2.OH$, in liquid styrax (p. 27).[2] The alcohols are obtained by the hydrolysis of the ethers and do not require to be separated, since the latter is converted into phenylpropyl alcohol by the action of sodium amalgam. It is

[1] Hofmann, *Ber. Deutsch. Chem. Ges.* viii. 66 ; xi. 329.

[2] Rügheimer, *Ann. Chem. Pharm.* clxxii. 122 ; Miller, *ibid.* clxxxviii. 201 ; Hatton and Hodgkinson, *Journ. Chem. Soc.* 1881, i. 319.

a thick, powerfully refractive liquid, which has a faint, characteristic odour, boils at 235° and does not solidify at —18°.

Primary phenylpropyl chloride, $C_6H_5.C_3H_6Cl$, is obtained by heating the alcohol with concentrated hydrochloric acid under pressure, and is a liquid, which has an odour resembling that of cymene, boils at 219° and is converted by boiling alcoholic potash into *ethyl phenylpropyl ether*, $C_6H_5.C_3H_6O.C_2H_5$, which boils at 220°.[1]

Primary phenylpropyl acetate, $C_6H_5.C_3H_6O.CO.CH_3$, is formed by the action of acetyl chloride on the alcohol as an almost odourless liquid, boiling at 244°—245°.

Phenylpropylamine, $C_6H_5.C_3H_6.NH_2$, is obtained when sodium amalgam is gradually added to an alcohol solution of cinnamylaldehydehydrazone which contains acetic acid:

$$C_6H_5.CH{=}CH.CH{=}N_2H.C_6H_5 + 6H = C_6H_5.CH_2.CH_2.CH_2.NH_2 + H_2N.C_6H_5.$$

It is separated from the aniline, which is simultaneously formed, by the method which has already been described in connection with secondary styrolamine. It is a liquid, which boils at 215°—216°, rapidly absorbs carbon dioxide from the air, and forms a strongly alkaline solution in water, in which it is only slightly soluble; it volatilizes when the aqueous solution is boiled and forms a vapour, which has an extremely penetrating odour.[2]

Methylbenzylcarbinol or *phenylisopropyl alcohol*, $C_6H_5.CH_2.CH(OH)CH_3$, is formed by the action of sodium amalgam and water on the corresponding ketone, and is a pleasant-smelling liquid, which boils at 215° and is converted into the chloride $C_6H_5.CH_2.CHCl.CH_3$, by heating with hydrochloric acid. This partially decomposes on distillation into hydrochloric acid and allylbenzene, which is also formed when the chloride is treated with alcoholic potash (Errera). The same chloride is also formed, together with the primary derivative, by the action of chlorine on boiling propylbenzene (see also p. 7).

Phenylisopropylamine, $C_6H_5.CH_2.CH(NH_2)CH_3$, is obtained by the action of bromine and caustic potash on phenylisobutyramide, $C_6H_5.CH_2CH(CH_3)CO.NH_2$ (see Part IV. p. 113). It is a strongly refractive liquid, and boils at 203°.[3]

[1] Errera, *Gaz. Chim. Ital.* xvi. 310.
[2] Tafel, *Ber. Deutsch. Chem. Ges.* xix. 1930.
[3] Edeleano, *ibid.* xx. 616.

Ethylphenylcarbinol, $C_6H_5.CH(OH)CH_2.CH_3$, has also been prepared from the corresponding ketone,[1] and boils at 215°—217°. It is converted by hydrochloric acid into the chloride, $C_6H_5.CHCl.CH_2.CH_3$, which boils at 200°—205°, but decomposes to a large extent into hydrochloric acid and allylbenzene. It is readily converted by silver acetate into the acetate, $C_6H_5.CH(OC_2H_3O)CH_2.CH_3$, a liquid which boils at 227° and has a fruity odour.

KETONES, $C_9H_{10}O$.

2363 *Ethylphenylketone* or *Propiophenone*, $C_6H_5.CO.C_2H_5$, has been prepared by Freund by the action of zinc ethyl on benzoyl chloride,[2] while Bechi obtained it by the gradual addition of sodium to a very dilute solution of ethyl iodide and benzoyl chloride.[3] Barry then prepared it by the distillation of a mixture of calcium propionate and calcium benzoate, and Pampel and Schmidt by the action of aluminium chloride on a mixture of benzene and propionyl chloride.[4] It is a liquid, which has a very pleasant odour, boils at 210°, does not combine with acid sodium sulphite and is oxidized by chromic acid solution to acetic acid and benzoic acid.

Nitropropiophenone, $C_6H_4(NO_2)CO.C_2H_5$, is formed when the ketone is brought into well-cooled fuming nitric acid. It crystallizes from alcohol in small, well-developed prisms, melting at 100°.

A syrupy *nitropropiophenone* is obtained at a higher temperature, so that this ketone behaves in a precisely similar manner to acetophenone.

Amidopropiophenone, $C_6H_4(NH_2)CO.C_2H_5$, is formed by the action of tin and hydrochloric acid on the alcoholic solution of the crystallized compound, and forms a syrup which smells of strawberries. Its hydrochloride is readily soluble in water and gives a granular crystalline platinichloride (Barry).

Methylbenzylketone, $C_6H_5.CH_2.CO.CH_3$, is obtained by the distillation of a mixture of barium acetate and barium phenylacetate,[5] as well as by the action of phenylacetyl chloride on zinc methyl.[6] It is a liquid, which has a pleasant odour, boils at

[1] Barry, *ibid.* vi. 1006 ; Errera, *loc. cit.*
[2] *Ann. Chem. Pharm.* cxviii. 20 ; Kalle, *ibid.* cxix. 166.
[3] *Ber. Deutsch. Chem. Ges.* xii. 463.
[4] *Ibid.* xix. 2896.
[5] Radziszewski, *ibid.* iii. 198.
[6] Popow, *ibid.* v. 500.

215°, readily combines with acid sodium sulphite and is oxidized by chromic acid solution to acetic and benzoic acids. When gently warmed with sulphuric acid, the sulphonic acid, $CH_3.CO.CH_2.C_6H_4.SO_3H$, is formed; on further heating however decomposition into acetic acid and benzylsulphonic acid takes place:[1]

$$C_6H_5.CH_2.CO.CH_3 + SO_2(OH)_2 = C_6H_5.CH_2.SO_2.OH + HO.CO.CH_3.$$

PHENYLPROPIONYL COMPOUNDS.

2364. The two phenylpropionic acids which can exist according to theory are both known:

a	*β*
CH_3	$CH_2.C_6H_5$
|	|
$CH—C_6H_5$	CH_2
|	|
CO_2H	CO_2H

The second of these has been obtained by the addition of hydrogen to cinnamic acid, $C_6H_5.CH{=}CH.CO_2H$, the constitution of which is accurately known, and it hence follows that the *a*-acid must possess the constitution which is ascribed to it above, this being further proved by the fact that it is oxidized in alkaline solution by potassium permanganate to atrolactic acid,[2] $CH_3.C(OH)(C_6H_5)CO_2H$, only tertiary hydrogen atoms being converted into hydroxyl in this way.[3]

a-Phenylpropionic acid was discovered by Kraut and named *blastophenylpropionic acid* (βλαστός, twig), while the isomeric acid was termed stichophenylpropionic acid (στίχος, a row).[4] Fittig and Wurster then investigated this acid more completely,[5] and named it *hydratropic acid*, since it may be obtained by the action of sodium amalgam and water on atropic acid, $CH_2{=}C(C_6H_5)CO_2H$, or the dibromohydratropic acid, $CH_2Br.CBr(C_6H_5)CO_2H$, which is formed by the combination

[1] Krekeler, *Ber. Deutsch. Chem. Ges.* xix. 2623.
[2] Ladenburg and Rügheimer, *ibid.* xiii. 373.
[3] Meyer and Baue, *ibid.* xii. 2238; v. Miller, *ibid.* xi. 1526 and 2216; xii. 1542; Tanatar, *ibid.* xii. 2293; xiii. 159.
[4] *Ann. Chem. Pharm.* cxlviii. 244.
[5] *Ibid.* cxcv. 164.

of bromine with the latter, atrolactic acid being also the final product in this case.

Hydratropic acid is a strongly refractive oily liquid, which has almost the same consistency as glycerol and becomes very viscous at −20° without solidifying. It boils at 264°—265°, is volatile with steam and is heavier than water, in which it is only very slightly soluble.

Calcium hydratropate, $(C_9H_9O_2)_2Ca + 2H_2O$, crystallizes from a hot solution on cooling in broad, opaque needles, which often unite to form large druses. If the solution be allowed to evaporate spontaneously however, long, lustrous, transparent, crystals, containing three molecules of water, are obtained.

Silver hydratropate, $C_9H_9O_2Ag$, separates from boiling water in scales.

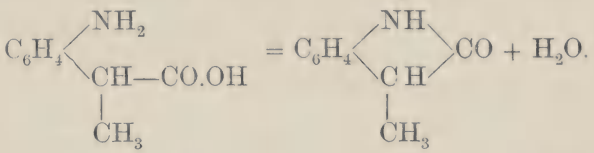
Paranitrohydratropic acid, $C_6H_4(NO_2)C_2H_4.CO_2H$, is formed together with the ortho-compound, from which it may be separated by means of its crystalline barium salt, which is scarcely soluble in absolute alcohol, while that of the ortho-acid forms a readily soluble, gummy mass.

Paranitrohydratropic acid separates from hot water in short, thick crystals, melting at 87°—88°, and is oxidized to paranitrobenzoic acid by chromic acid solution.

Orthonitrohydratropic acid forms readily-soluble crystals, melting at 110°, and is oxidized by potassium permanganate to orthonitrobenzoic acid.

Paramidohydratropic acid, $C_6H_4(NH_2)C_2H_4.CO_2H$, crystallizes from water in thick, yellowish plates, which melt at 128°. It forms unstable metallic salts, but stable compounds with acids.

Atroxindol, C_9H_9NO, is homologous with oxindol and is formed by the reduction of orthonitrohydratropic acid, the orthamido acid passing immediately into the lactone:



It forms crystals, which melt at 119°, are slightly soluble in cold, more readily in hot water and commence to sublime at 100°. When freshly prepared it has a fæcal odour, which changes to that of flowers after recrystallization.[1]

[1] Trinius, *Ann. Chem. Pharm.* ccxxvii. 262.

β-Phenylpropionaldehyde, $C_6H_5.C_2H_4.CHO$, was prepared by Etard in a similar manner to phenyl acetaldehyde (p. 10), by decomposing the compound which is formed between propylbenzene and chromyl chloride with water.[1] It is a liquid, which boils at 208° and forms a crystalline compound with acid sodium sulphite.

2365 *β-Phenylpropionic acid.* This acid, which is known by many different names, was discovered by Erlenmeyer and Alexejew and named *homotoluic acid.* Their investigation was undertaken with the intention of decomposing cinnamic acid, which Bertagnini had obtained synthetically by heating benzaldehyde with acetylchloride, into benzaldehyde and acetaldehyde. In order to accomplish this, they acted upon it with sodium amalgam and water and thus found that cinnamic acid combines with hydrogen.[2]

Popow prepared the same acid by heating cinnamic acid with hydriodic acid,[3] and Schmitt, who named it *cumoylic acid*, by the action of sodium amalgam and water on phenyldibromopropionic acid, $C_6H_5.CHBr.CHBr.CO_2H$, which is formed by the combination of cinnamic acid with bromine.[4] Swarts, who obtained it by the action of sodium and carbon dioxide on bromostyrolene (*α*-phenylbromethylene) (p. 33), gave it the name of *hydrocinnamic acid*,[5] which has been universally accepted. Fittig and Kiesow prepared its nitril by the action of potassium cyanide on styrolyl chloride (p. 8), and converted this without purification into hydrocinnamic acid.[6] It has also been obtained by Lydia Sesemann, who termed it benzylacetic acid, together with dibenzylacetic acid, $(C_6H_5.CH_2)_2CH.CO_2H$, by heating crude sodaceto-acetic ether with benzylchloride and hydrolysing the product with potash.[7] Rügheimer has also prepared it by the oxidation of phenylpropyl alcohol,[8] and Conrad by heating benzylmalonic acid,[9] $C_6H_5.CH_2.CH(CO_2H)_2$. It has been observed among the products of the pancreatic fermentation of albuminoids[10] and the products of putrefaction of the brain of the ox (p. 12).[11]

[1] *Ann. Chim. Phys.* [5] xxii. 254.
[2] *Ann. Chem. Pharm.* cxxi. 375; Erlenmeyer, *ibid.* cxxxvii. 327.
[3] *Zeitschr. Chem.* 1865, 111.
[4] *Ann. Chem. Pharm.* cxxvii. 329.
[5] *Ibid.* cxxxvii. 230.
[6] *Ibid.* clvi. 249.
[7] *Ber. Deutsch. Chem. Ges.* vi. 1085; x. 758.
[8] *Ann. Chem. Pharm.* clxxii. 122.
[9] *Ber. Deutsch. Chem. Ges.* xii. 752.
[10] H. and E. Salkowski, *Ber. Deutsch. Chem. Ges.* xii. 107 and 649.
[11] Stöckli, *Journ. Prakt. Chem.* [2] xxiv. 17.

In order to prepare hydrocinnamic acid, 1 part of cinnamic acid is heated for an hour with 4 parts of hydriodic acid of boiling point 127° and a little amorphous phosphorus. The acid separates out on cooling in a solid cake, which is dissolved in ammonia and precipitated by hydrochloric acid in the filtered solution. The hydrocinnamic acid which separates is then distilled; the almost pure compound, containing only a small quantity of an oily substance, passes over at about 280°.[1]

Hydrocinnamic acid possesses a characteristic goat-like odour, melts at 47·5° and solidifies on cooling in long, brittle needles; it boils at 280°, is readily volatile with steam, dissolves in 168 parts of water at 20°, more readily in hot water, and separates in oily drops when the solution is slightly cooled. It is readily soluble in alcohol, from which it separates in indistinct, apparently monosymmetric crystals. A mixture of hydrocinnamic and phenylacetic acids, which is obtained by the putrefaction of albuminoids, has a lower melting point than either of its constituents. Such a mixture containing 35 per cent. of hydrocinnamic acid melts at 21°.[2]

This acid yields benzoic acid on oxidation, accompanied by some benzaldehyde and an oily body, which smells like sage and does not combine with acid sodium sulphite. This was only obtained in small quantity and could not be further investigated (Erlenmeyer).

Potassium hydrocinnamate, $C_9H_9O_2K$, forms broad, lustrous, soluble needles.

Calcium hydrocinnamate, $(C_9H_9O_2)_2Ca + 2H_2O$, crystallizes in broad, lustrous needles, which form stellate groups, or, when the solution is gradually evaporated, in large, almost rectangular tablets.

Barium hydrocinnamate, $(C_9H_9O_2)_2Ba + 2H_2O$, forms broad needles, which are tolerably soluble in water.

Silver hydrocinnamate, $C_9H_9O_2Ag$, crystallizes from hot water in nacreous plates.

Ferric chloride produces a dun-yellow-coloured precipitate in the solutions of the neutral salts.

Methyl hydrocinnamate, $C_9H_9O_2(CH_3)$, is a liquid, which boils at 238°—239° and has a characteristic odour.

Ethyl hydrocinnamate, $C_9H_9O_2(C_2H_5)$, is a powerfully refractive

[1] Gabriel and Zimmermann, *Ber. Deutsch. Chem. Ges.* xiii. 1680.
[2] H. Salkowski, *ibid.* xviii. 321.

liquid, which possesses an overpowering odour resembling that of pineapple and boils at 247° – 249°.

Benzyl hydrocinnamate, $C_9H_9O_2(CH_2.C_6H_5)$, is formed by heating benzyl acetate with sodium (Pt. IV. p. 97):

$$4\left|\begin{matrix}CH_3\\CO_2.CH_2.C_6H_5\end{matrix}\right. + Na_2 = 2\left|\begin{matrix}CH_2.CH_2.C_6H_5\\CO_2.CH_2.C_6H_5\end{matrix}\right. + 2\left|\begin{matrix}CH_3\\CO_2Na\end{matrix}\right. + H_2.$$

It is a liquid, which has an aromatic odour, boils at 290° and is not easily decomposed by alkalis. When heated with sodium, it decomposes into toluene and cinnamic acid, so that these products are always formed in the preparation of the ether:[1]

$$\left|\begin{matrix}CH_2.CH_2.C_6H_5\\CO_2.CH_2.C_6H_5\end{matrix}\right. = \left|\begin{matrix}CH{=}CH.C_6H_5\\CO_2H\end{matrix}\right. + CH_3.C_6H_5.$$

β-Phenylpropionitril or *Hydrocinnamonitril*, $C_6H_5.C_2H_4.CN$, is the chief constituent of the ethereal oil of watercress (*Nasturtium officinale*); 600 kilogs. of this plant, gathered when in flower, yielded 40 grams. of the oil, from which the pure nitril was obtained by fractional distillation. It boils at 261° and is converted into the acid by fusion with caustic potash.[2]

2366 *Halogensubstitution products of hydrocinnamic acid* have been prepared by heating the corresponding derivatives of cinnamic acid with hydriodic acid and phosphorus. These compounds have a similar smell to that of hydrocinnamic acid, but in a less degree.[3]

Chlorohydrocinnamic Acids, $C_6H_4Cl.C_2H_4.CO_2H$.

	Melting-point.
Ortho, needles or plates	96·5°
Meta, small, snow-white plates	77°—78°
Para, crystals	124°

Bromohydrocinnamic Acids, $C_6H_4Br.C_2H_4.CO_2H$.

	Melting-point.
Ortho, serrate scales	97°—99°
Meta, short, thick prisms	75°
Para, flat needles	136°

[1] Conrad and Hodgkinson, *Ann. Chem. Pharm.* cxciii. 298.
[2] Hofmann, *Ber. Deutsch. Chem. Ges.* vii. 520.
[3] Gabriel, *ibid.* xv. 2291; Gabriel and Herzberg, *ibid.* xvi. 2036.

The last of these has been obtained directly from hydrocinnamic acid.[1]

IODOHYDROCINNAMIC ACIDS, $C_6H_4I.C_2H_4.CO_2H$.

	Melting-point.
Ortho, plates	102°—103°
Meta, small plates	65°— 66°
Para, white prisms	140°—141°

Paranitrohydrocinnamic acid, $C_6H_4(NO_2)C_2H_4.CO_2H$, is formed together with the ortho-acid when hydrocinnamic acid is dissolved in well-cooled fuming nitric acid.[2] It is scarcely soluble in cold and only slightly in boiling water, from which it crystallizes in small, flat, very lustrous needles, while it separates from alcohol in very fine needles, melting at 163° - 164°.[3] Chromic acid solution oxidizes it to paranitrobenzoic acid.

Metanitrohydrocinnamic acid has been prepared from metanitroparamidohydrocinnamic acid by means of the diazo-reaction. It crystallizes from hot water in long, lustrous yellow needles, which melt at 117° - 118°.[4]

Orthonitrohydrocinnamic acid has been obtained in the pure state from orthonitroparamidohydrocinnamic acid. It separates from hot water in small, yellow crystals, melting at 113°.[5]

Dinitrohydrocinnamic acid, $C_6H_3(NO_2)_2C_2H_4.CO_2H$ (4 : 2 : 1) is best prepared by dissolving 6 grams. of hydrocinnamic acid in 60 grams. of cold fuming nitric acid and then adding 40 grams. of sulphuric acid. The mixture is allowed to cool and is then poured into cold water, the dinitro-acid separating out after some time. It crystallizes from hot water in long, yellowish, compact needles or short, thick prisms, melting at 126·5°.[6]

Paramidohydrocinnamic acid, $C_6H_4(NH_2)C_2H_4.CO_2H$, is obtained by pouring a hot ammoniacal solution of paranitrohydrocinnamic acid into an ammoniacal solution of the calculated quantity of ferrous sulphate :

$$C_6H_4(NO_2)C_2H_4.CO_2H + 6FeSO_4 + 12NH_3 + 16H_2O = C_6H_4(NH_2)C_2H_4.CO_2H + 3Fe_2(OH)_6 + 6(NH_4)_2SO_4.$$

[1] Glaser and Buchanan, *Zeitschr. Chem.* 1869, 193 ; Gabriel and Zimmermann, *Ber. Deutsch. Chem. Ges.* xiii. 1680.
[2] Buchanan and Glaser, *Zeitschr. Chem.* 1869, 193.
[3] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clxiii. 132.
[4] Gabriel and Steudemann, *Ber. Deutsch. Chem. Ges.* xv. 842.
[5] Gabriel and Zimmermann, *ibid.* xiii. 1680.
[6] Gabriel and Zimmermann, *loc. cit.* and *Ber. Deutsch. Chem. Ges.* xii. 600.

The mixture is boiled for five minutes, filtered and evaporated to a small volume, the acid being deposited in crystalline crusts, which melt at 131°. It forms unstable metallic salts, while its compounds with acids crystallize well (Buchanan and Glaser; Gabriel and Steudemann).

Paramido-orthonitrohydrocinnamic acid, $C_6H_3(NH_2)(NO_2)C_2H_4.CO_2H$, was prepared by Gabriel and Zimmermann from dinitrohydrocinnamic acid by reduction with hot ammonium sulphide. It crystallizes from water in flat needles or broad tablets, which resemble potassium dichromate in colour and melt at 137°—139°. The hydrochloride forms colourless crystals.

Paramidometanitrohydrocinnamic acid is obtained by heating paramidohydrocinnamic acid with acetic anhydride, nitrating the acetyl derivative, which is thus formed, and decomposing the product with hydrochloric acid. It forms short, thick, orange-red crystals, melting at 145° (Gabriel and Steudemann).

Metamidohydrocinnamic acid, $C_6H_4(NH_2)C_2H_4.CO_2H$, is formed by the reduction of the corresponding nitro-acid and separates from hot water in octohedral or acute rhombic crystals, melting at 84°—85°. Its hydrochloride crystallizes in scales or broad needles.

2367 *Hydrocarbostyril*, C_9H_9NO, is the lactame of orthoamidohydrocinnamic acid and is the homologue of oxindol; it is formed by the reduction of orthonitrohydrocinnamic acid, the amido-acid losing the elements of water immediately on formation:

$$C_6H_4\begin{cases}CH_2.CH_2.CO.OH\\NH_2\end{cases} = C_6H_4\begin{cases}CH_2—CH_2\\NH—CO\end{cases} + H_2O.$$

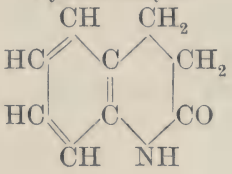
It is best prepared from the ethyl ether of orthonitro-cinnamic acid, $C_6H_4(NO_2)C_2H_2.CO_2H$, by saturating its alcoholic solution with hydrochloric acid and adding zinc dust, the mixture being kept well-cooled, until an energetic evolution of hydrogen takes place. The addition of water then precipitates the pure hydrocarbostyril.[1]

Buchanan and Glaser obtained it by the reduction of crude nitrohydrocinnamic acid with tin and hydrochloric acid,[2] while Gabriel and Zimmermann prepared it from the pure ortho-acid. It crystallizes from alcohol in prisms, which melt at 163° and are readily soluble in hydrochloric acid. It is converted by phosphorus chloride into dichloroquinoline (Baeyer),

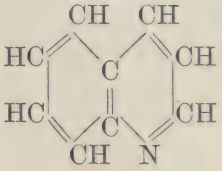
[1] Friedländer and Weinberg, *Ber. Deutsch. Chem. Ges.* xv. 1423.
[2] *Loc. cit.*; Baeyer, *Ber. Deutsch. Chem. Ges.* xii. 46.

which can readily be reduced to quinoline, C_9H_7N, a base which is obtained by heating many alkaloids with caustic potash. The constitution of these compounds is shown by the following formulæ:

Hydrocarbostyril.



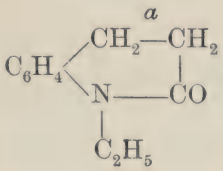
Quinoline.

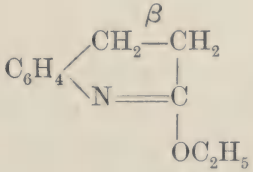


α-Ethylhydrocarbostyril, $C_9H_8(NC_2H_5)O$, is formed when hydrocarbostyril is heated with ethyl iodide and alcoholic potash, or when an alkaline solution of ethylorthonitrocinnamic acid is heated with sodium amalgam. It is a thick, oily liquid, which has a faint but pleasant smell of flowers, dissolves in strong hydrochloric acid and is reprecipitated by water.[1]

β-Ethylhydrocarbostyril, $C_9H_8N(OC_2H_5)$, is formed by the reduction of ethylcarbostyril and is a mobile liquid, which has a penetrating but sweet smell and is decomposed by hydrochloric acid into alcohol and hydrocarbostyril.[2]

The isomerism of these compounds is explained by the following formulæ:





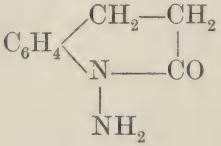
Paramidohydrocarbostyril, $C_9H_8(NH_2)NO$, is formed by the reduction of dinitrohydrocinnamic acid, and crystallizes from hot water in long needles or short, thick prisms, which melt at 211°. Its hydrochloride crystallizes in fine, white needles (Gabriel and Zimmermann).

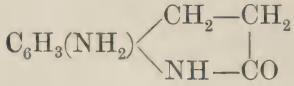
Hydrazinhydrocinnamic anhydride, $CH_{10}N_2O$, This lactame, which Fischer and Kuzel have named *amidohydrocarbostyril*, is formed when an alkaline solution of hydrazinesulphocinnamic acid is treated with sodium amalgam and then heated with hydrochloric acid. The lactame is precipitated by the addition of

[1] Friedländer and Weinberg, *Ber. Deutsch. Chem. Ges.* xv. 2103.
[2] *Ibid.* xv. 1424.

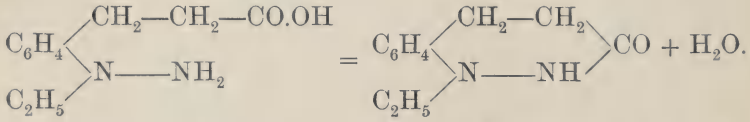
hydrochloric acid and crystallizes from hot water in small plates, which melt at 143°. Its hydrochloride crystallizes in prisms. When an acid solution of the base is treated with sodium nitrite, hydrocarbostyril separates out. On heating the lactame with ethyl iodide and alcohol, *ethylamidohydrocarbostyril*, $C_9H_9O_2N$—$NH(C_2H_5)$, is obtained in colourless crystals, melting at 74°; it is a base which forms readily soluble salts.[1]

The isomerism of the lactame with paramidohydrocarbostyril is rendered evident by the following formulæ:





Ethylhydrocarbazostyril, $C_9H_9O_2N_2(C_2H_5)$. The product of the action of sodium amalgam on an alcoholic solution of ethylamidocinnamic acid is ethylamidohydrocinnamic acid, which is converted into the nitroso-compound by sodium nitrite in acid solution. This is reduced by zinc dust and acetic acid to ethylamidohydrocinnamic acid, which decomposes on evaporation into water and the lactame:



Ethylhydrocarbazostyril crystallizes from hot water in long needles, which melt at 165·5° and can be volatilized without decomposition. It dissolves in cold hydrochloric acid and is reprecipitated by water; when it is heated with the acid, however, it is reconverted into the hydrazine acid.[2]

HYDROXYPHENYLPROPIONIC ACIDS, $C_6H_4(OH)C_2H_4.CO_2H$.

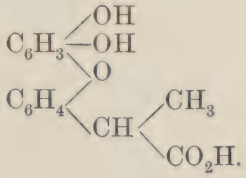
2368 *Phloretic acid* was first prepared by boiling phloretin with caustic potash.[3] Its constitution was determined by Trinius, who obtained it from paramidohydratropic acid by means

[1] *Ann. Chem. Pharm.* ccxxi. 282. [2] Fischer and Kuzel, *ibid*, ccxxi. 293.
[3] Hlasiwetz, *Journ. Prakt. Chem.* lxvii. 109; lxxii. 395; Schiff, *Ann. Chem. Pharm.* clxxii. 356.

of the diazo-reaction, and named it *parahydroxyhydratropic acid*,[1] $C_6H_4(OH)CH(CH_3)CO_2H$. It crystallizes from ether in monosymmetric prisms or groups resembling wavellite, is tolerably soluble in cold, readily in hot water, has an acid, astringent taste and melts at 129°. On heating with baryta it decomposes into carbon dioxide and phlorol or β-ethylphenol (p. 4), while it is resolved into acetic acid and parahydroxybenzoic acid by fusion with caustic potash.[2]

Phloretin, $C_{15}H_{14}O_5$, is formed when phloridzin is boiled with dilute sulphuric acid,[3] and crystallizes in small plates, melting at 180°. It dissolves in every proportion in alcohol, and is readily soluble in alkalis, but almost insoluble in cold water and only very slightly soluble in boiling water. On boiling with alkalis, it decomposes into phloretic acid and phloroglucinol, while on heating with acetyl chloride it forms a diacetyl compound.[4]

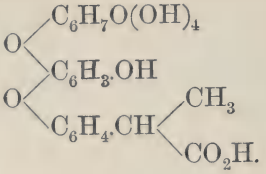
It has therefore, according to Schiff, the following constitution:



Phloridzin, $C_{21}H_{24}O_{10}+2H_2O$, was discovered by Koningk in the root bark (φλοιός, bark; ῥίζα, root) of the apple, pear, plum and cherry tree.[5] It is best obtained, according to Stas,[6] from that of the apple tree by extraction with warm, dilute alcohol. It crystallizes in silky needles, which have a sweet taste, followed by a bitter after-taste, melt at 108° with loss of water, solidify at a higher temperature and finally fuse at 170°—171°, with formation of phloretin and glucosan (Schiff). It dissolves in 1000 parts of cold water and in every proportion in boiling water. On boiling with dilute acids it decomposes into phloretin and a glucose, which Hesse has named phlorose,[7] $C_6H_{12}O_6$, but which has been shown by Rennie to be identical with dextrose.[8] It also combines with bases and yields a pentacetyl derivative

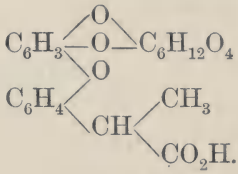
[1] *Ann. Chem. Pharm.* ccxxvii. 268.
[2] Barth, *ibid.* clii. 96; Barth and Schreder, *Ber. Deutsch. Chem. Ges.* xii. 1259.
[3] Stas, *Ann. Chem. Pharm.* xxx. 200; Schiff, *ibid.*; *loc. cit.*
[4] Schiff, *Ann. Chem. Pharm.* clvi. 1.
[5] *Ibid.* xv. 75 and 258.
[6] *Ibid.* xxx. 192.
[7] *Ibid.* clxxvi. 114; cxcii. 173.
[8] *Journ. Chem. Soc.* 1887, i. 634.

on heating with acetic anhydride, and has therefore the following constitution (Schiff):



According to Rochleder, the leaves of the apple tree contain isophloridzin,[1] but Schiff found that this is identical with phloridzin.[2]

Glycyphillin, $C_{21}H_{24}O_9$, occurs in the leaves of *Smilax glycyphilla*, which is employed in Australia, where the plants are abundant, as an anti-scorbutic, &c. It separates from aqueous ether in crystals, containing three molecules of water, and from solution in water in thin, brittle, four-sided prisms, containing four and a half molecules of water, has a sweet taste resembling that of licorice and decomposes on heating with dilute acids into phloretin and isodulcite,[3] so that it must possess the following constitution:—



2369 *Hydroparacumaric acid* or *Parahydroxyhydrocinnamic acid*, $C_6H_4(OH)C_2H_4.CO_2H$, was obtained by Hlasiwetz by treating paracumaric acid, $C_6H_4(OH)CH=CH.CO_2H$, with sodium amalgam,[4] and was prepared by Buchanan and Glaser by the action of nitrous acid on paramidohydrocinnamic acid.[5] It is, however, best prepared from parahydroxyphenyl-*a*-amidopropionic acid or tyrosine, $C_6H_4(OH)CH_2.CH(NH_2)CO_2H$, 6 grms. of which are ground up in 5 litres of water and allowed to stand for two days at the temperature of an incubator in contact with a few flakes of putrefied pancreas. The liquid is then evaporated to a tenth of its bulk, acidified with sulphuric acid and extracted with ether. The residue obtained by the evaporation of the

[1] *Zeitschr Chem.* 1868, 711. [2] *Ann. Chem. Pharm.* ccxxix. 371.
[3] Wright and Rennie, *Journ. Chem. Soc.* 1881, i. 237; Rennie, *ibid.* 1886, i. 857.
[4] *Ann. Chem. Pharm.* cxlii. 358. [5] *Zeitschr. Chem.* 1869, 197.

ether is extracted with water and treated with lead acetate solution to remove fatty acids, the filtrate being then freed from lead by means of sulphuretted hydrogen and evaporated to a syrup, from which the hydroparacumaric acid crystallizes.[1] Twelve parts of this were obtained from 20 parts of tyrosine.[2] It has also been detected in human urine, in the pus from a case of peritonitis[3] and among the products of the putrefaction of flesh.[4]

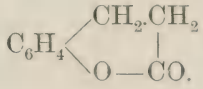
It crystallizes in monosymmetric prisms, which melt at 128°—129°.[5] On further putrefaction with pancreas, it decomposes into parahydroxyphenylacetic acid, paracresol and phenol, and is resolved into parahydroxybenzoic acid and acetic acid by fusion with caustic potash.[6]

Its substitution products have been investigated by Stöhr, who also found that it behaves towards Millon's reagent in precisely the same way as tyrosine.

Ethyl hydroparacumarate, $C_6H_4(OH)C_2H_4.CO_2.C_2H_5$, is an oily liquid, which smells like rhubarb root, in which it is perhaps present (Stöhr).

Methylhydroparacumaric acid, $C_6H_4(OCH_3)C_2H_4.CO_2H$, is obtained by the action of water and sodium amalgam on methylparacumaric acid. It forms feathery crystals or long, white needles, melting at 102°.[7]

Melilotic acid or *Hydrocumaric acid* was discovered by Zwenger and Bodenbender in the common melilot (*Melilotus officinalis*),[8] and is formed by the action of water and sodium amalgam on cumaric acid or orthohydroxycinnamic acid[9] and cumarin.[10] It crystallizes from water in long needles, and from benzene in thin, transparent prisms, which melt at 83° and decompose on distillation into water and the anhydride. This is also formed when the acid is brought into contact with hydrobromic acid,[11] and has the following constitution:



[1] Baumann, *Ber. Deutsch. Chem. Ges.* xii. 1451. [2] *Ibid.* xiii. 279.
[3] Baumann, *Hoppe-Seyler's Zeitschr.* iv. 307.
[4] E. and H. Salkowski, *Ber. Deutsch. Chem. Ges.* xiii. 190.
[5] Stöhr, *Ann. Chem. Pharm.* ccxxv. 57.
[6] Barth and Schreder, *Ber. Deutsch. Chem. Ges.* xii. 1259.
[7] Perkin, *Journ. Chem. Soc.* 1877, i. 411; Eigel, *Ber. Deutsch. Chem. Ges.* xx. 2527.
[8] *Ann. Chem. Pharm.* cxxvi. 262.
[9] Herzfeld and Tiemann, *Ber. Deutsch. Chem. Ges.* x. 286.
[10] Zwenger, *Ann. Chem. Pharm. Suppl.* v. 122.
[11] Hochstetter, *ibid.* ccxxvi. 355.

It crystallizes in tablets, melts at 25°, boils at 272° and smells like cumarin, into which it is converted by heating with bromine (Hochstetter).

The *melitolol*, $C_9H_8O_2$, which Phipson obtained by distilling blossoming melilot, with water, is probably identical with this substance. It forms an oily liquid, smelling like the plant, and yields melilotic acid on boiling with caustic potash.[1]

Methylmelilotic acid, $C_6H_4(OCH_3)C_2H_4CO_2H$, was obtained by Perkin by the action of sodium amalgam on aqueous solutions of *a*- and *β*-sodium methyl cumarate. It separates from hot alcohol in transparent crystals, which resemble those of Glauber's salt, and melt at 92°.[2]

DIHYDROXYPHENYLPROPIONIC ACIDS, $C_6H_3(OH)_2C_2H_4.CO_2H$.

2370 *Hydrocaffeic acid* (4 : 3 : 1) is formed by the action of sodium amalgam and water on caffeic acid, $C_6H_3(OH)_2CH{=}CH.CO_2H$. It forms rhombic crystals, which are readily soluble in water. Its constitution corresponds to that of protocatechuic acid; like this, it gives a deep green colouration with ferric chloride, which is converted into dark red by the addition of sodium carbonate. It is precipitated by lead acetate and readily reduces Fehling's solution and ammoniacal silver solution.[3]

The following ethers have been prepared from the corresponding derivatives of caffeic acid:[4]

	Melting-point
Hydroferulic acid, $C_6H_3(OH)(OCH_3)C_3H_5O_2$, microscopic tablets	89°—90°
Isohydroferulic acid, $C_6H_3(OCH_3)(OH)C_3H_5O_2$ fine needles	146°
Dimethylhydrocaffeic acid, $C_6H_3(OCH_3)_2C_3H_5O_2$, fine needles	96°—97°
Methylenehydrocaffeic acid,[5] $CH_2\langle O \rangle C_6H_3.C_3H_5O_2$, long needles	84°

[1] *Compt. Rend.* lxxxvi. 830.
[2] *Journ. Chem. Soc.* 1881, i. 415.
[3] Hlasiwetz, *Ann. Chem. Pharm.* cxlii. 353.
[4] Nagai and Tiemann, *Ber Deutsch. Chem. Ges.* xi. 650.
[5] Lorenz, *ibid.* xiii. 756; Regel, *ibid.* xx. 421.

Hydro-umbellic acid (6 : 2 : 1) is formed by the action of sodium amalgam and water on umbelliferon, which is the anhydride of umbelliferonic acid, isomeride of caffeic acid. It forms granular crystals, which are only slightly soluble in water and commence to lose water and decompose at 110°. It is not precipitated by lead acetate, but reduces silver solution and Fehling's solution and gives a green colouration with ferric chloride. It is converted into resorcinol by fusion with caustic potash.[1]

PHENYLHYDROXYPROPIONIC ACIDS.

2371 *Atrolactic acid* or *α-Phenyl-α-propionic acid*, $C_6H_5.C(CH_3)(OH)CO_2H$, was obtained by Wurster and Fittig by boiling *α*-bromohydratropic acid with sodium carbonate solution.[2] It is also formed by the oxidation of hydratropic acid with potassium permanganate,[3] and when hydrochloric acid is added to well-cooled acetophenone containing some moistened potassium cyanide, the nitril being first formed as an oily liquid, which dissolves in the excess of hydrochloric acid with formation of the acid and separation of ammonium chloride.[4]

Atrolactic acid crystallizes in broad needles or rhombic tablets, containing half a molecule of water, which is lost over sulphuric acid. The anhydrous acid melts at 93°—94°; it is readily soluble in water and is not decomposed by boiling with baryta water, but is resolved into atropic acid and water by boiling hydrochloric acid.

Its salts have been investigated by Fittig and Wurster.

Ethylatrolactic acid, $C_6H_5.C(OC_2H_5)(CH_3)CO_2H$. The nitril, $C_6H_5.C(OC_2H_5)(CH_3)CN$, is formed when methylphenylmethylene dichloride, $C_6H_5.CCl_2.CH_3$, which is obtained by the action of phosphorus chloride or acetophenone, is brought into a solution of potassium cyanide in dilute alcohol, and is converted into the acid by boiling with baryta water.[5] The acid may also be obtained by passing hydrochloric acid into an alcoholic solution of bromo-

[1] Hlasiwetz and Grabowski, *Ann. Chem. Pharm.* cxxxix. 102.
[2] *Ibid.* cxcv. 145.
[3] Ladenburg and Rügheimer, *Ber. Deutsch. Chem. Ges.* xiii. 374.
[4] Spiegel, *ibid.* xiv. 235 and 1352.
[5] Ladenburg and Rügheimer, *ibid.* xiii. 2041.

hydropäic acid, treating the ether, $C_6H_5.CBr(CH_3)CO_2.C_2H_5$, with sodium ethylate and decomposing the product by boiling with baryta water.[1]

Ethylatrolactic acid is tolerably soluble in hot water and crystallizes from petroleum-spirit in small prisms, which melt at 59·5°—62°, and are converted into atropic acid by boiling with hydrochloric acid.

α-Chlorhydratropic acid or *α-Phenyl-α-chloropropionic acid*, $C_6H_5.C(CH_3)Cl.CO_2H$, is formed when atrolactic acid is dissolved in concentrated hydrochloric acid, and separates out after some hours. It may be obtained from petroleum-ether in crystals, which melt at 73°—74° and decompose at 110° with evolution of gas. It does not yield styrolene when boiled with sodium carbonate solution.[2]

α-Phenyl-α-bromopropionic acid or *α-Bromohydratropic acid*, $C_6H_5.CBr(CH_3)CO_2H$, is obtained by the combination of atropic acid, $C_6H_5.C(CO_2H)=CH_2$, with hydrobromic acid,[3] *β*-bromohydratropic acid being simultaneously formed (Merling). It may be prepared pure by the action of fuming hydrobromic acid on atrolactic acid; it is readily soluble in carbon disulphide, less readily in petroleum-ether, and crystallizes from a mixture of these in tablets, melting at 93°—94°.

α-Phenyl-α-amidopropionic acid or *α-Amidohydratropic acid*, $C_6H_5.C(NH_2)(CH_3)CO_2H$. When the nitril of ethylatrolactic acid is heated to 60°—80° with alcoholic ammonia, phenylamidopropionitril is formed as an oily liquid. If it be treated with cold fuming hydrochloric acid and then heated with dilute hydrochloric acid and alcohol, the hydrochloride of the amido-acid, which crystallizes in concentrically grouped needles, is formed. If ammonia be added to the alcoholic solution of this salt, the free acid is obtained. It is insoluble in alcohol and crystallizes from a concentrated aqueous solution in feathery needles, which have a satin lustre and sublime at about 260° without melting. When the aqueous solution of the hydrochloride is heated with sodium nitrite, pure atrolactic acid is formed and can thus be prepared in considerable quantity.[4]

Dibromatrolactic acid, $C_6H_5.C(OH)CHBr_2.CO_2H$, is gradually

[1] Rügheimer, *Ber. Deutsch. Chem. Ges.* xiv. 446.
[2] Merling, *Ann. Chem. Pharm.* ccix. i.
[3] Fittig and Kast, *loc. cit.*
[4] Tiemann and Köhler, *Ber. Deutsch. Chem. Ges.* xiv. 1980.

precipitated when dibromopyroracemic acid is brought into twenty parts of sulphuric acid and benzene added:

$$C_6H_6 + CO\begin{<}CHBr_2\\CO_2H\end{} = C_6H_5.C\begin{<}CHBr_2\\OH\\CO_2H\end{}.$$

It is only slightly soluble in water and crystallizes from chloroform in lustrous needles and from benzene in long, four-sided prisms, which melt at 167°. It is converted into atrolactic acid by the action of water and sodium amalgam, while it yields carbon dioxide, hydrobromic acid and benzoylmethyl bromide on boiling with water:[1]

$$C_6H_5(COH)\begin{<}CHBr_2\\CO_2H\end{} = CO_2 + HBr + C_6H_5.CO.CH_2Br$$

2372 *Tropic acid* or *α-Phenyl-β-hydroxypropionic acid*, $C_6H_5.CH(CH_2.OH)CO_2H$. The isomeric alkaloids *atropine* and *hyoscyamine*, $C_{17}H_{23}NO_3$, which are contained in deadly nightshade (*Atropa belladonna*), the thorn-apple (*Datura stramonium*), the henbane (*Hyoscyamus niger*), and others of the Solanaceae, decompose on boiling with baryta water into *tropin* and tropic acid,[2] which is also formed when β-chlorohydropäic acid is heated to 120°—130° with sodium carbonate solution,[3] or boiled with potassium carbonate solution.[4] It crystallizes from hot water in needles and on the spontaneous evaporation of its aqueous solution in tablets, which melt at 117°—118°. It is not affected by water at 130°, but is converted by continued boiling with baryta water into atropic acid, $C_6H_5.C(CO_2H)=CH_2$.

α-Phenyl-β-chloropropionic acid or *β-Chlorohydropäic acid*, $C_6H_5.CH(CH_2Cl)CO_2H$, was obtained by Ladenburg, who treated tropic acid with phosphorus chloride and decomposed the product with water,[5] and has been prepared by Spiegel by heating atrolactonitril to 130° with fuming hydrochloric acid, the atrolactic acid which is first formed decomposing into water and atropic acid, the latter of which then combines with hydrochloric acid. The chlorinated acid is therefore also readily

[1] Böttinger, *Ber. Deutsch. Chem. Ges.* xiv. 1235.
[2] Lossen, *Ann. Chem. Pharm.* cxxxviii. 233; Kraut, *ibid.* cxlviii. 238; Ladenburg, *Ber. Deutsch. Chem. Ges.* xiii. 254.
[3] Spiegel, *ibid.* xiv. 235 and 1352. [4] Merling, *Ann. Chem. Pharm.* ccix. 1.
[5] *Ber. Deutsch. Chem. Ges.* xii. 947.

obtained when atropic acid is heated to 100° with hydrochloric acid saturated at 0° (Merling). It is insoluble in cold, readily in hot water and crystallizes from carbon disulphide in small tablets, which melt at 87°—88° and volatilize at a higher temperature with decomposition, forming a vapour which attacks the eyes violently.

α-Phenyl-β-bromopropionic acid, $C_6H_5.CH(CH_2Br)CO_2H$, is formed by heating atropic acid with hydrobromic acid and crystallizes from carbon disulphide in small prisms, melting at 93°—94° (Merling).

α-Phenyl-β-amidopropionic acid, $C_6H_5.CH.(CH_2.NH_2)CO_2H$, is formed by the action of cold ammonia on the brominated acid, and crystallizes from hot water in lustrous plates or fine needles, melting at 169·5°.

α-Phenyl-lactic acid or *β-Phenyl-α-propionic acid*, $C_6H_5.CH_2.CH(OH)CO_2H$, was obtained by Erlenmeyer by the action of hydrocyanic and hydrochloric acids on phenylacetaldehyde,[1] while Conrad prepared it by heating benzylhydroxylmalonic acid, $C_6H_5.CH_2.C)OH)(CO_2H)_2$, to 160°—180°.[2] It crystallizes from water in large, thick, lustrous prisms, which melt at 98° and decompose on further heating into formic acid and phenylacetaldehyde.

α-Phenyl-lactonitril, $C_6H_5.CH_2.CH(OH)CN$, is formed when freshly prepared phenylacetaldehyde is treated with anhydrous hydrocyanic acid and crystallizes in stellate or warty groups of small needles, which melt at 57°—58° and decompose at 100° with evolution of hydrocyanic acid.

β-Phenyl-α-amidopropionic acid or *Phenylalanine*, $C_6H_5.CH_2.CH(NH_2)CO_2H$. The nitril of this acid is formed by the action of alcoholic ammonia on the preceding compound and is converted into the free acid by heating with concentrated hydrochloric acid.[3] It is also found, accompanied by other amido-acids, in the young shoots of *Lupinus luteus*.[4] It crystallizes from hot water in short, distorted prisms, and from dilute alcohol in small plates with a satin lustre, which are decomposed on heating with formation of styrolylamine (p. 7). Its compounds with acids and bases crystallize well.

Paranitrophenylalanine, $2C_6H_4(NO_2)CH_2.CH(NH)_2)CO_2H + 3H_2O$, is formed when concentrated nitric acid is added to a

[1] *Ber. Deutsch. Chem. Ges.* xiii. 303.
[2] *Ann. Chem. Pharm.* ccix. 247.
[3] Erlenmeyer and Lipp, *ibid.* ccxix. 186.
[4] Schulze and Barbieri, *Ber. Deutsch. Chem. Ges.* xiv. 1785.

solution of phenylalanine in sulphuric acid, and crystallizes from water in stellate groups of prisms, which effloresce in the air. It is oxidized to paranitrobenzoic acid by chromic acid solution.

Paramidophenylalanine, $C_6H_4(NH_2)CH_2CH(NH_2)CO_2H+H_2O$, is obtained by the reduction of the nitro-compound with tin and hydrochloric acid, and is also formed when the ethyl ether of dinitrocinnamic acid, $C_6H_4(NO_2)CH{=}C(NO_2)CO_2H$, is treated first with tin and hydrochloric acid and then with sodium amalgam and water.[1] It crystallizes from hot water in lustrous, brittle prisms, which have a sweet taste. Its hydrochloride, $C_9H_{12}N_2O_2(HCl)_2$, forms small lustrous prisms (Erlenmeyer and Lipp).

2373 *Tyrosine*, $C_6H_4(OH)CH_2.CH(NH_2)CO_2H$, was discovered by Liebig, who obtained it by fusing freshly prepared cheese (*τύρος*) with caustic potash.[2] It may be obtained in a similar manner, together with leucine, from other albuminoids, horn, feathers, hair, etc., and also by boiling them with dilute sulphuric or hydrochloric acid, and is also formed by the putrefaction of such substances.[3] It occurs both in the animal and vegetable kingdoms and is found in cochineal,[4] crayfish, spiders, caterpillars and moths, but not in butterflies, which only contain leucine.[5] The latter also accompanies it in the liver during certain diseases.[6] Schulze and Barbieri detected it along with glutamic and aspartic acids in the young shoots of the gourd [7] and Lippmann obtained the same compounds and leucine from beet molasses.[8]

The composition of tyrosine was determined by Warren de la Rue and Hinterberger, while its physical and chemical properties were first studied by Strecker [9] and then more thoroughly by Städeler.

The former of these made the suggestion "that tyrosine, like glycocoll and leucine, is a copula occurring in many animal substances."

According to Städeler it has undoubtedly a similar constitution to these compounds, since it combines both with acids and bases, but differs from them in being a weak dibasic acid, while

[1] Freidländer and Mähly, *Ann. Chem. Pharm.* ccxxix. 226.
[2] *Ibid.* lvii. 127; lxii. 269.
[3] Bopp, *ibid.* lxix. 20; Hinterberger, *ibid.* lxxi. 74; Leyer and Köller, *ibid.* lxxxiii. 332; Städeler, *ibid.* xci. 12; Müller, *Journ. Prakt. Chem.* lv. 162 and 447.
[4] Warren de la Rue, *Ann. Chem. Pharm.* lxiv. 36.
[5] Fterichs and Städeler, *ibid.* cxvi. 57.
[6] *Jahresb. Chem.* 1856, 702.
[7] *Ber. Deutsch. Chem. Ges.* xi. 710.
[8] *Ibid.* xvii. 2835.
[9] *Ann. Chem. Pharm.* lxxiii. 70.

these are both monobasic. Schmitt and Nasse considered it to be ethylamidosalicylic acid and endeavoured, but without success, to prepare it synthetically. They found however, as a proof of the accuracy of their view, that it decomposes on heating into carbon dioxide and hydroxyethylaniline[1] (Pt. III. p. 206). Barth then showed that tyrosine is resolved into ammonia, acetic acid, and parahydroxybenzoic acid by fusion with caustic potash, and therefore looked upon it as ethylamido-parahydroxybenzoic acid.[2] Hüfner however proved that on heating with hydriodic acid, ammonia and no ethylamine is formed, and Barth concluded from this that it is a parahydroxyphenylamidopropionic acid, without being able to decide whether it is derived from phloretic or hydroparacumaric acid.[3] Beilstein and Kuhlberg considered it as a derivative of the latter and gave it the formula $C_6H_4(OH)C_2H_3(NH_2)CO_2H$, the position of the amido-group being undecided,[4] but were, like Barth, unable to prepare it synthetically. Ladenburg, who started with the view that tyrosine is ethyloxyparamidobenzoic acid, $C_6H_4NH(OC_2H_5)CO_2H$, prepared the latter, but found it to be different from tyrosine.[5] Erlenmeyer and Lipp however succeeded in preparing it by adding a solution of the calculated quantity of sodium nitrite to a well-cooled solution of paramidophenylalanine in dilute sulphuric acid, and in this way proved it to be parahydroxyphenylalanine or parahydroxyphenyl-*a*-amidopropionic acid.[6]

In order to prepare tyrosine, according to the method given by Hinterberger and Städeler, 6 kilogr. of horn shavings, which give the best yield, are boiled for 16 hours with 12 kilos. of sulphuric acid and 60 litres of water, the volume of the liquid being kept constant by the repeated addition of small quantities of water. The liquid is then neutralized with milk of lime, filtered and the residue extracted twice with water. The solution is then evaporated to half its bulk, acidified with sulphuric acid, filtered and made into a thin paste with lead carbonate. The filtrate is treated with sulphuretted hydrogen and concentrated. The tyrosine, which crystallizes out, is separated from the thick mother liquor, which deposits crystals of leucine, accompanied by a little tyrosine, after standing for some months. These may easily be separated since tyrosine is

[1] *Ann. Chem. Pharm.* cxxxiii. 212.
[2] *Ibid.* cxxxvi. 111.
[3] *Ibid.* clii. 100.
[4] *Ibid.* clxiii. 142.
[5] *Ber. Deutsch. Chem. Ges.* vi. 129.
[6] *Ann. Chem. Pharm.* ccxix. 161.

insoluble in alcohol.[1] One hundred parts of horn shavings yield 3·6 parts of tyrosine and 10 parts of leucine.

Tyrosine crystallizes in lustrous, stellate or fascicular groups of needles (Fig. 1), which dissolve in 150 parts of boiling water and in 2400 parts of cold water (Erlenmeyer and Lipp). It is scarcely soluble in cold alcohol and is insoluble in ether. The decompositions which it undergoes by heating and fusing with caustic potash have already been stated, as well as the fact that it is converted into hydroparacumaric acid by the pancreatic putrefaction; this acid is also formed by the putrefaction of

Fig. 1.

albuminoids, but must be looked upon as derived from tyrosine, which is the first product. A transient red colouration is produced when tyrosine is dissolved in a few drops of sulphuric acid at a gentle heat. If the solution be diluted with water, neutralized with barium carbonate, boiled, filtered and ferric chloride gradually added to the filtrate, a beautiful violet colouration, due to the tyrosinesulphonic acid present, is produced.[2]

If a neutral solution of mercuric nitrate (Millon's reagent) be added to an aqueous solution of tyrosine as long as a yellowish

[1] Baeyer, *Zeitschr. Chem.* 1867, 436.
[2] Piria, *Ann. Chem. Pharm.* lxxxii. 251; Städeler, *ibid.* cxvi. 66.

white precipitate is formed, which becomes dark coloured and much denser after being repeatedly boiled with a few drops of dilute nitric acid (a few drops of fuming acid in a test tube full of water).[1]

Tyrosine has a perfectly neutral reaction, but combines with acids; the hydrochloride, $C_9H_{11}NO_3.ClH + 2H_2O$, crystallizes in scales or long, flat, lustrous prisms, which are decomposed by water.

2374 Since it is simultaneously a phenol and a monobasic acid, it contains two hydrogen atoms which can be replaced by metals. Its salts have been investigated by Städeler.

When tyrosine is dissolved in warm saturated baryta water, the compound $C_9H_9NO_3Ba + 2H_2O$ separates out as a heavy precipitate, consisting of prismatic crystals.

Copper tyrosine, $(C_9H_{10}NO_3)_2Cu$, is a very characteristic salt, and is formed when copper hydroxide is added to a boiling aqueous solution of tyrosine. The splendid blue solution soon deposits dark blue needles, consisting of monosymmetric prisms, which are insoluble in alcohol and decompose on boiling with water, with separation of the black oxide.[2]

Silver tyrosine, $C_9H_{10}NO_3Ag$, is obtained by the addition of silver nitrate to a boiling solution of tyrosine to which some ammonia has been added. It forms a sandy precipitate, consisting of short, microscopic prisms, which is tolerably stable towards light. A similar precipitate containing half a molecule of water is often formed (Erlenmeyer and Lipp), and was sometimes observed by Städeler.

When a saturated ammoniacal solution of tyrosine is added to silver nitrate, a heavy amorphous precipitate of the salt $C_9H_9NO_3Ag_2 + H_2O$ is formed; it retains its water at 110° and deflagrates violently when further heated.

Nitrotyrosine, $C_9H_{10}(NO_2)NO_3$. The nitrate of this is formed by dissolving tyrosine in nitric acid (Strecker). Ammonia added to its solution precipitates the free nitrotyrosine, which is only slightly soluble in hot water, and crystallizes on cooling in light yellow needles, which have a slightly bitter, but not acid, taste, and form a deep red coloured solution in alkalis (Städeler).

Dinitrotyrosine, $C_9H_9(NO_2)_2NO_3$, is obtained by the evaporation of nitrotyrosine nitrate with nitric acid; it crystallizes in lustrous, golden-yellow plates, which are slightly soluble in water, readily in alcohol, have an acid but not bitter taste and do not combine

[1] Hoffmann, *Ann. Chem. Pharm.* lxxxvii. 124; L. Meyer, *ibid.* cxxxii. 156.
[2] Hofmeister, *ibid.* clxxxix. 24.

with acids. It is a strong dibasic acid, the yellow and red salts of which deflagrate on heating (Städeler).

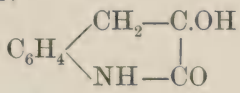
Amidotyrosine, $C_9H_{10}(NH_2)NO_3$, was obtained by Beyer by the reduction of nitrotyrosine; it is a crystalline powder, which is readily soluble in water and slightly in alcohol, and is a di-acid base.

Tyrosinesulphonic acid, $C_9H_{10}NO_3.SO_3H + 2H_2O$, forms a starchy powder, consisting of microscopic crystals, which crystallizes from a hot aqueous solution in anhydrous, slightly soluble crusts. Ferric chloride produces a violet colouration in the aqueous solution (Städeler).

Parahydroxy-α-phenyl-lactic acid, $C_6H_4(OH)CH_2.CH(OH)CO_2H + H_2O$, is formed in the preparation of tyrosine from amidophenylalanine when more than the calculated amount of sodium nitrite is employed. It crystallizes in needles, which become anhydrous at 100° and melt at 144°

Nitrophenyl-lactyl nitrate, $C_6H_4(NO_2)CH_2(CH_2O.NO_2)CO_2H$, is obtained by the nitration of *α*-phenyl-lactic acid, and crystallizes in needles. It yields paranitrobenzoic acid on oxidation, and is converted by reduction into *paramido-α-phenyl-lactic acid*, $C_6H_4(NH_2)CH_2(CH.OH)CO_2H$, which is isomeric with tyrosine. It crystallizes in fine needles, which have an acid reaction and taste, melt with decomposition at 188°—189°, are more soluble in water and alcohol than tyrosine and do not give Piria's reaction. Its hydrochloride is a crystalline mass, which is readily soluble in water.

Hydroxyhydrocarbostyril, $C_9H_9NO_2$. A syrupy ortho-compound is formed by the nitration of *α*-phenyl-lactic acid, which yields hydroxyhydrocarbostyril on reduction. It crystallizes from alcohol in white, lustrous plates, which sublime when heated in open vessels, but melt at 197°—198° when heated in capillary tubes. Its constitution is expressed by the following formula (Erlenmeyer and Lipp):



2375 *β-Phenyl-lactic acid* or *β-Phenyl-β-hydroxypropionic acid*, $C_6H_5.CH(OH)CH_2.CO_2H$, was obtained by Glaser by the action of sodium amalgam on a solution of chloro- or bromo-phenyl-lactic acid.[1] It is also formed when *β*-phenyl-*β*-bromopropionic

[1] *Ann. Chem. Pharm.* cxlvii. 78.

acid is boiled with water,[1] and crystallizes in lustrous needles or prisms, which are readily soluble in cold water and in every relation in boiling water, melt at 93° and decompose on further heating or on boiling with baryta water into water and cinnamic acid. Its salts have been investigated by Glaser, and also by Fittig and Kast.[2]

β-Phenyl-β-chloropropionic acid, $C_6H_5.CHCl.CH_2.CO_2H$, was prepared by Glaser by the addition of concentrated hydrochloric acid to a concentrated solution of β-phenyl-lactic acid. It is also formed when a solution of cinnamic acid in glacial acetic acid is saturated with hydrochloric acid and allowed to stand for some time.[3] It crystallizes from alcohol in nacreous plates, which melt at 126° and decompose into hydrochloric acid and cinnamic acid a few degrees above this temperature.

β-Phenyl-β-bromopropionic acid, $C_6H_5.CHBr.CH_2.CO_2H$, which has been prepared by Glaser in a similar manner to the chlorine compound, is also readily formed when cinnamic acid is allowed to stand for several days in contact with hydrobromic acid, saturated at 0° (Fittig and Binder), or more rapidly when it is heated with a solution of hydrobromic acid in glacial acetic acid.[4] It is very soluble in alcohol and ether, and decomposes when moist on gentle heating. It crystallizes from hot carbon disulphide in nacreous plates and from chloroform in monosymmetric prisms.[5] On boiling with ten parts of water, β-phenyl-lactic acid and cinnamic acid are formed, together with a little styrolene, which forms the chief product when sodium carbonate solution is employed.

β-Phenyl-β-iodopropionic acid, $C_6H_5.CHI.CH_2.CO_2H$, is formed by the action of hydriodic acid on β-phenyl-lactic acid (Glaser) and on cinnamic acid (Fittig and Binder). It separates from hot carbon disulphide in small, lustrous crystals, which melt with decomposition at 119°—120°. It behaves towards water and sodium carbonate solution in a similar manner to the bromine compound, but in this case styrolene is formed in predominating amount.

β-Phenyl-β-amidopropionic acid, $C_6H_5.CH(NH_2)CH_2.CO_2H$, is formed, together with cinnamic acid and styrolene, when the brominated acid is brought into ammonia at a temperature

[1] Fittig and Binder, *Ann. Chem. Pharm.* cxcv. 131.
[2] *Ibid.* ccvi. 26.
[3] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xiv. 1867.
[4] Anschütz and Kinnicut, *ibid.* xi. 1221.
[5] Bodewig, *ibid.* xii. 538.

of 0°.[1] It is only slightly soluble in cold, readily in hot water, and crystallizes in large, monosymmetric prisms,[2] melting at 120°—121°. It does not combine with bases, but forms salts with acids, its hydrochloride crystallizing in lustrous prisms. On boiling with hydrochloric acid, it yields cinnamic acid and ammonium chloride.

KETONIC ACIDS, $C_8H_7O.CO_2H$.

2376 *Benzoylacetaldehyde*, $C_6H_5.CO.CH_2.CHO$. When equal molecules of ethyl formate and acetophenone are added to an ice-cold solution of sodium in twenty to thirty parts of alcohol, a granular crystalline precipitate is gradually formed:

$$C_6H_5.CO.CH_3 + CHO.OC_2H_5 + NaO.C_2H_5 = C_6H_5CO.CHNa.CHO + 2HO.C_2H_6.$$

If this be dissolved in water and treated with acetic acid, the aldehyde is obtained as an oily, unstable liquid, the alcoholic solution of which produces a deep red colouration with ferric chloride. Copper acetate gives a light green precipitate, consisting of fine needles of $(C_9H_7O_2)_2Cu$, which soon change into flat, dark green, glittering prisms. When an aniline salt is added to the solution of the sodium compound *benzoylethidene-aniline*, $C_6H_5.CO.CH_2.CH{=}NC_6H_5$ (Pt. IV. p. 140), separates out, and may be obtained from hot alcohol, in which it is readily soluble, in small yellow plates or short prisms, melting at 140°—141°. Similar compounds are formed with other primary amido-bases.[3]

Benzoylacetic acid, $C_6H_5.CO.CH_2.CO_2H$, is formed when phenyl-propiolic acid is dissolved in sulphuric acid and the liquid poured upon ice after standing for some hours:

$$C_6H_5.C{\equiv}C.CO_2H + H_2O = C_6H_5.CO.CH_2.CO_2H.$$

It may be more readily obtained from its ethyl ether by dissolving it in dilute caustic soda, acidifying with sulphuric acid after twenty-four hours and extracting with ether. The acid

[1] Posen, *Ann. Chem. Pharm.* cxcv. 144.
[2] Calderon, *Jahresb. Chem.* 1880, 372.
[3] Claisen and Fischer, *Ber. Deutsch. Chem. Ges.* xx. 2191.

is left on evaporation as a crystalline mass, which crystallizes from benzene in small needles, melting with evolution of carbon dioxide at 103°—104°. It is slightly soluble in cold, more readily in hot water, and decomposes when strongly treated by itself or with sulphuric acid into methylphenylketone and carbon dioxide. Its alcoholic or hot aqueous solution is coloured violet by ferric chloride.[1]

Ethyl benzoylacetate, $C_6H_5.CO.CH_2.CO_2C_2H_5$, is obtained in a similar manner from ethyl propiolate. It may be synthetically prepared in the following manner. The nitrite of ethyl amid-acetate, $NO_2.NH_3.CH_2.CO_2.C_2H_5$, is formed by the action of silver nitrite on the hydrochloride, and crystallizes in transparent, colourless prisms, which soon decompose with formation of ethyl diazo-acetate, $N_2CH.CO_2.C_2H_5$, a golden yellow, volatile, and explosive liquid, which possesses a characteristic odour. When this is heated with benzaldehyde in presence of toluene, it combines with evolution of nitrogen and formation of ethyl benzoylacetate :[2]

$$C_6H_5.CHO + \begin{matrix} N \\ | \\ N \end{matrix}\!\!>\!CH.CO_2.C_2H_5 = C_6H_5.CO.CH_2.CO_2.C_2H_5 + N_2.$$

A better yield of the ether is obtained when equal molecules of sodium ethylate, free from alcohol, and ethyl benzoate are heated on the water-bath until a compact cake has been formed ; this is heated for fifteen hours with an excess of ethyl acetate, and then treated with glacial acetic acid and water, the oil which separates being dried and distilled under diminished pressure. A little aceto-acetic ether passes over first, followed by unaltered ethyl benzoate and finally benzoylacetic ether, a small quantity of dehydrobenzoylacetic acid being left behind.[3] Ethyl benzoylacetate is also readily formed by the action of sodium on a mixture of ethyl benzoate and ethyl acetate.[4] It is a strongly refractive liquid, which boils with decomposition at 268°—270°, has a pleasant smell resembling that of aceto-acetic ether and decomposes on boiling with dilute sulphuric acid into carbon dioxide, alcohol and methylphenylketone. The

[1] Baeyer, *Ber. Deutsch. Chem. Ges.* xv. 2705 ; Baeyer and Perkin, *ibid.* xvi. 2125 ; Perkin, *Journ. Chem. Soc.* 1884, i. 170 ; 1885, i. 240.

[2] Curtius, *Ber. Deutsch. Chem. Ges.* xvii. 953 ; Curtius and Buchner, *ibid.* xviii. 2371.

[3] Claisen and Lowman, *ibid.* xx. 651.

[4] Wislicenus, *ibid.* xx. 654.

alcoholic solution gives a violet-red colouration with ferric chloride.

The hydrogen of the methylene group in ethyl benzoylacetate, like that in aceto-acetic ether, is replaceable by metals, alcohol radicals, etc. When the alkaline solution is treated with sodium amalgam, β-phenyl-lactic acid is formed.

Sodium ethyl benzoylacetate, $C_6H_5.CO.CHNa.CO_2.C_2H_5$, separates out in long, silky needles, when sodium ethylate is added to the ether. It is insoluble in cold water, but is decomposed on boiling.

Ethyl isonitrosobenzoylacetate, $C_6H_5.CO.C(NOH)CO_2.C_2H_5$, is formed when sodium nitrite and then dilute sulphuric acid are added to the alkaline solution of the ether. It crystallizes from alcohol in long needles, which melt at 120° – 121° and form a yellow solution in alkalis.

Paranitrobenzoylacetic acid, $C_6H_4(NO_2)CO.CH_2.CO_2H$, is obtained by dissolving paranitrophenylpropiolic acid in 80—85 per cent. sulphuric acid and allowing the solution to stand at 35°—40° for fifteen hours. It is then poured on to ice and the acid extracted with ether. It crystallizes from benzene in microscopic needles and from hot water in four-sided tablets, which melt at 135° and simultaneously decompose into carbon dioxide and paranitro-acetophenone, the same decomposition being effected by boiling with water. Its alcoholic or warm aqueous solution gives a deep reddish brown colouration with ferric chloride.

Ethyl nitrobenzoylacetate, $C_6H_4(NO_2)CO.CH_2.CO_2.C_2H_5$, is formed by passing hydrochloric acid into a mixture of the acid with absolute alcohol, and crystallizes in yellow needles or from a mixture of benzene and petroleum-spirit in transparent, monosymmetric prisms, melting at 74°—76°. Its sodium compound crystallizes in orange-yellow needles, which have a very bitter taste and can be recrystallized from hot water. When nitrogen trioxide is passed into a solution of the ether, the isonitroso-compound, $C_6H_4(NO_2)CO.C(NOH)CO_2.C_2H_5$, is formed and crystallizes from alcohol in colourless needles, which form a deep yellow solution in alkalis.[1]

Benzoylacetonitril or *Cyanacetophenone*, $C_6H_5.CO.CH_2.CN$, is formed when ethyl benzoylcyanacetate, $C_6H_5.CO.CH(CN)CO_2.C_2H_5$, is boiled with water, and crystallizes in needles which melt at 80·5°. Its ammoniacal solution gives a precipitate of

[1] Perkin and Bellenot, *Journ. Chem. Soc.* 1886, i. 440.

$C_6H_5.CO.CHAg.CN$ with silver nitrate, which rapidly alters in the light. When it is boiled with concentrated caustic potash solution or is allowed to stand in contact with an excess of hydrochloric acid, it decomposes into benzoic acid, acetic acid and ammonia. If its alcoholic solution be saturated with hydrochloric acid at 0°, the *hydrochloride of benzoyl acetimido-ether*, $C_6H_5.CO.CH_2.C(OC_2H_5)NH.ClH$, separates out in needles. The free ether, which is prepared from this salt, forms needles or quadratic tablets, which melt at 89·5° and are converted into ethyl benzoylacetate by heating with alcohol and hydrochloric acid.[1]

2377 *Alphatoluylformic acid* or *Benzylglyoxylic acid*, $C_6H_5.CH_2.CO.CO_2H$. When hippuric acid is heated with benzaldehyde and acetic anhydride, *benzoylamidocinnamic acid* is formed:

$$\begin{array}{l} C_6H_5 \\ | \\ CHO \\ \\ CH_2.NH.CO.C_6H_5 \\ | \\ CO_2H \end{array} = \begin{array}{l} C_6H_5 \\ | \\ CH \\ \| \\ C.NH.CO.C_6H_5 \\ | \\ CO_2H \end{array} + H_2O.$$

This is converted by the further elimination of water into the anhydride, which crystallizes from alcohol in yellow needles, melting at 164°—165°, and yields the acid again on heating to 100° with dilute hydrochloric acid. The free acid is scarcely soluble in water and crystallizes in lustrous prisms resembling those of hippuric acid, which melt with decomposition at 225° and are converted into benzylglyoxylic acid by boiling with caustic potash solution:[2]

$$\begin{array}{l} C_6H_5 \\ | \\ CH \\ \| \\ CNH.CO.C_6H_5 \\ | \\ CO_2H \end{array} + 2H_2O = \begin{array}{l} C_6H_5 \\ | \\ CH_2 \\ | \\ CO \\ | \\ CO_2H \end{array} + HO.CO.C_6H_5 + NH_3.$$

It is also obtained when sodium is added to a mixture of ethyl oxalate with ether and ethyl phenylacetate gradually added; the ethyl ether of phenyloxalacetic acid is first formed and is then

[1] Haller, *Compt. Rend.* ci. 1270; civ. 1448.
[2] Plöchl, *Ber. Deutsch. Chem. Ges.* xvi. 2815.

decomposed in the following manner by boiling with dilute sulphuric acid:[1]

$$\begin{array}{l} C_6H_5 \\ | \\ CH{-}CO_2.C_2H_5 \\ | \\ CO \\ | \\ CO_2.C_2H_5 \end{array} + 2H_2O = \begin{array}{l} C_6H_5 \\ | \\ CH_2 \\ | \\ CO \\ | \\ CO_2H \end{array} + CO_2 + 2HO.C_2H_5.$$

Benzylglyoxylic acid is only slightly soluble in cold, somewhat more readily in hot water and readily in alcohol. It crystallizes from chloroform in small plates, which have a satin lustre and melt at 154°—155° with evolution of carbon dioxide. Its alcoholic solution is coloured deep green by ferric chloride and gives the same reaction as phenylglyoxylic acid with sulphuric acid and benzene containing thiophene.[2] As a ketonic acid it forms compounds with hydroxylamine and phenylhydrazine; water and sodium amalgam convert it into α-phenyl-lactic acid.

Orthohydroxybenzylglyoxylic acid, $C_6H_4(OH)CH_2.CO.CO_2H$, is prepared from hippuric acid and salicylaldehyde in a similar manner to the preceding compound. It crystallizes from hot water in flat needles or prisms and gives a deep green colouration with ferric chloride. On heating with dilute sulphuric acid it is converted into the anhydride, which has been named *oxycumarin* by Plöchl and Wolfram:

$$C_6H_4\left\langle\begin{array}{l} CH_2{-}CO \\ \qquad\quad | \\ OH \quad CO.OH \end{array}\right. = C_6H_4\left\langle\begin{array}{l} CH_2{-}CO \\ \qquad\quad | \\ O{-}{-}CO \end{array}\right. + H_2O.$$

It crystallizes from alcohol in lustrous prisms, melting at 152°—153°.

Orthohydroxybenzylglycolic acid or *Salicyl-lactic acid*, $C_6H_4(OH)CH_2.CH(OH)CO_2H$, is formed by the action of sodium amalgam and water on the preceding compound, and is a readily soluble syrup. Its salts however crystallize well.[3]

[1] W. Wislicenus, *Ber. Deutsch. Chem. Ges.* xx. 589.
[2] E. Erlenmeyer, Jun. *ibid.* xix. 2576.
[3] Plöchl and Wolfram, *ibid.* xviii. 1179.

PHENYLPROPENYL COMPOUNDS.

2378 *Phenylglycerol* or *Styceral*, $C_6H_5.CH(OH)CH(OH)CH_2.OH$, was prepared by Grimaux from its dibromohydrin by heating to 150°—165° with water and a little silver acetate. It is a gum like mass, which has a bitter taste, dissolves readily in water and alcohol, is insoluble in ether and decomposes on heating.[1]

Phenylpropenyldibromohydrate or *Styceroldibromohydrin*, $C_6H_5.CHBr.CHBr.CH_2.OH$, is obtained by the addition of bromine to a cooled solution of cinnamyl alcohol in chloroform. It is readily soluble in alcohol and ether and crystallizes in needles or tablets, melting at 74°.

Phenylpropenyl tribromide or *Styceroltribromohydrin*, $C_6H_5.CHBr.CHBrCH_2Br$, is formed by the combination of bromine with cinnyl bromide or by the repeated distillation of the preceding compound with hydrobromic acid. It crystallizes from ether in tablets, which melt at 96·5°.

Phenylpropenylacetodibromohydrin, $C_6H_5.CHBr.CHBr.CH_2.O.C_2H_3O$, is the product of the action of acetyl chloride on the dibromohydrin and crystallizes from ether in oblique prisms, melting at 85°—86°.[2]

PHENYLDIHYDROXYPROPIONIC ACIDS.

2379 *Phenylglyceric acid* or *Styceric acid*, $C_6H_5.CH(OH)CH(OH)CO_2H$, was first prepared from its ethyl dibenzoyl ether by heating with alcoholic potash.[3] It is also formed when *a*-phenylchlorolactic acid, $C_6H_5.CH(OH)CHCl.CO_2H$, is heated with caustic soda solution,[4] phenylacetaldehyde being simultaneously formed (p. 9). It crystallizes from ether, in which it is only slightly soluble, in lustrous plates, which melt with decomposition at 143°—144°.

[1] Grimaux, *Bull. Soc. Chim.* xx. 120. [2] Grimaux, *loc. cit.*
[3] Anschütz and Kinnicut, *Ber. Deutsch. Chem. Ges.* xi. 1219 ; xii. 538.
[4] Lipp, *ibid.* xvi. 1287.

Dibenzoylstyceric acid, $C_6H_5(CH.O.CO.C_6H_5)_2CO_2H$, is obtained by heating the acid with benzoyl chloride, and crystallizes from benzene in small needles (Lipp).

Ethyl dibenzoylstycerate, $C_6H_5(CH.O.CO.C_6H_5)_2CO_2C_2H_5$, is the product of the action of silver benzoate on ethyl phenyldibromopropionate in presence of toluene, from which it crystallizes on evaporation in well developed, monosymmetric crystals.

Paranitrostyceric acid, $C_6H_4(NO_2)CH(OH)CH(OH)CO_2H$, is formed when paranitrophenylglycidic acid is boiled with dilute sulphuric acid, and crystallizes from hot water in distorted plates, which melt at 167°—168°.[1]

β-Phenyldichloropropionic acid, $C_6H_5.CHCl.CHCl.CO_2H$, was prepared by Glaser by the action of fuming hydrochloric acid on phenylchlorolactic acid,[2] $C_6H_5.CH(OH)CHCl.CO_2H$, while Erlenmeyer obtained it by passing chlorine into a solution of cinnamic acid in carbon disulphide.[3] It crystallizes in lustrous plates, which melt at 162°—164°, with simultaneous discolouration, and are insoluble in water, but gradually decompose into carbon dioxide and *α*-phenylchlorethylene (p. 32) on boiling with water or on standing in the cold with sodium carbonate solution.

β-Phenyldibromopropionic acid, $C_6H_5.CHBr.CHBr.CO_2H$, is obtained by the action of bromine vapour on cinnamic acid,[4] as well as by treating phenylbromolactic acid with fuming hydrobromic acid.[5] In order to prepare it, cinnamic acid is dissolved in carbon disulphide and a solution of bromine in carbon disulphide gradually added, the acid being thus precipitated.[6] It forms small plates or monosymmetric crystals, which readily dissolve in ether, melt at 195° and readily decompose slightly above this temperature. On boiling with water, phenylbromolactic acid, cinnamic acid, *α*-phenylbromethylene and carbon dioxide are formed. This decomposition is also brought about by cold sodium carbonate solution, but is delayed by an excess of this reagent.[7]

Glaser obtained an isomeric acid in the form of a smeary crystalline mass by the action of bromine on hydrocinnamic

[1] Lipp, *Ber. Deutsch. Chem. Ges.* xix. 2645.
[2] *Ann. Chem. Pharm.* cxlvii. 96.
[3] *Ber. Deutsch. Chem. Ges.* xiv. 1867.
[4] Schmitt, *Ann. Chem. Pharm.* cxxvii. 320.
[5] Glaser, *ibid.* cxlvii. 91.
[6] Fittig and Binder, *ibid.* cxcv. 140.
[7] Fittig and Kast, *ibid.* ccvi. 33.

acid. This substance decomposes on boiling with water with formation of phenylacetaldehyde :[1]

$$C_6H_5.CH_2.CBr_2.CO_2H + H_2O =$$
$$C_6H_5.CH_2.CHO + CO_2 + 2HBr.$$

Ethers of Phenyldibromopropionic acid are best obtained by the addition of bromine to the corresponding cinnamic ethers. Like the acids they form well developed, monosymmetric crystals.[2]

	Melting-point.
Methyl phenyldibromopropionate, $C_9H_7Br_2O_2(CH_3)$.	117°
Ethyl phenyldibromopropionate, $C_9H_7Br_2O_2(C_2H_5)$.	69°
Propyl phenyldibromopropionate, $C_9H_7Br_2O_2(C_3H_7)$.	23°

Phenylchlorohydroxypropionic acid or *α-Phenylchlorolactic acid*, $C_6H_5.CH(OH)CHCl.CO_2H + H_2O$, is formed by the addition of hypochlorous acid to cinnamic acid.[3] In order to prepare it, chlorine is passed into a cooled solution of cinnamic acid and sodium carbonate, or, more advantageously, a solution of sodium hypochlorite is added to one of potassium cinnamate, *α*-phenylchlorethylene being simultaneously formed.[4] It is tolerably soluble in cold, in every proportion in boiling water, and crystallizes in six-sided plates, which lose their crystal-water over sulphuric acid and then melt at 104°.

Orthonitrophenylchlorolactic acid, $C_6H_4(NO_2)CH(OH)CHCl.CO_2H$, is prepared by passing chlorine into an alkaline solution of orthonitrocinnamic acid, and is precipitated by petroleum-ether from its solution in benzene as a crystalline mass, which melts at 119°—120 and is converted into indol by treatment with sodium amalgam or caustic soda and ferrous sulphate (p. 36).[5]

α-Paranitrophenylchlorolactic acid, $C_6H_4(NO_2)CH(OH)CHBr.CO_2H$, is obtained in a similar manner from paranitrocinnamic acid, and crystallizes from water in rhombic plates, melting at 165°.[6] Its barium salt can be boiled with water without undergoing decomposition.

β-Paranitrophenylchlorolactic acid, $C_6H_4(NO_2)(CHCl)CH(OH)CO_2H$, is formed by the combination of hydrochloric acid with

[1] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xiii. 308.
[2] Anschütz and Kinnicut, *loc. cit.*
[3] Glaser, *Ann. Chem. Pharm.* cxlvii. 79.
[4] Erlenmeyer and Lipp, *ibid.* ccxix. 183.
[5] Baeyer, *Ber. Deutsch. Chem. Ges.* xiii. 2261.
[6] Beilstein and Kuhlberg, *Ann. Chem. Pharm.* clxiii. 42.

paranitrophenylglicidic acid, and forms small crystals, melting at 167°—168°. The barium salt decomposes on boiling with water into carbon dioxide, barium chloride and paranitrophenylacetaldehyde (p. 10).[1]

α-Phenylbromolactic acid, $C_6H_5.CH(OH)CHBr.CO_2H + H_2O$, is formed when phenyldibromopropionic acid is boiled with water, and by the addition of hypobromous acid to cinnamic acid. It crystallizes from hot water in plates, which lose their crystal-water on heating and then melt at 125°.[2]

β-Phenylbromolactic acid, $C_6H_5.CHBr.CH(OH)CO_2H$, is prepared by the action of fuming hydrobromic acid on styceric acid and has not been fully described.[3]

α-Phenyliodolactic acid, $C_6H_5.CH(OH)CHI.CO_2H$, is obtained by bringing cinnamic acid into an aqueous solution of iodine chloride. It separates from benzene in large crystals, which melt at 137°—139° with decomposition.[4]

2380 *Phenylglycidic acid*, $C_6H_5.C_2H_2O.CO_2H$, is formed when *α*-phenylchlorolactic acid or the corresponding bromine compound is treated with alcoholic potash (Glaser):

$$\begin{array}{l} C_6H_5.CH.OH \\ \quad\quad | \\ CO_2H.CHBr \end{array} = \begin{array}{l} C_6H_5.CH \\ \quad\quad | \quad\diagdown O. \\ CO_2H.CH \end{array}$$

Acids precipitate it as an oily liquid, which solidifies at 0° to minute, lustrous scales and decomposes at the ordinary temperature into phenylacetaldehyde and carbon dioxide (Erlenmeyer).

Orthonitrophenylglycidic acid, $C_6H_4(NO_2)C_2H_2O.CO_2H$, is prepared by the action of alcoholic potash on orthonitrophenyl-lactic acid,[5] or by boiling the latter with sodium carbonate solution.[6] It crystallizes in flat needles and melts with decomposition at 110°, a portion being thus converted into indigo-blue (Baeyer).

Paranitrophenylglycidic acid was obtained by Erlenmeyer as a by-product in the preparation of paranitrochlorophenyl-lactic acid; it is also formed by the action of alcoholic potash on the latter, and crystallizes in splendid tablets, which have a satin lustre and melt at 186°—188°. It combines with hydrochloric acid to form *β*-paranitrophenylchlorolactic acid.[7]

[1] Lipp, *Ber. Deutsch. Chem. Ges.* xix. 2646.
[2] Glaser, *Ann. Chem. Pharm.* cxlvii. 84; Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xiii. 310; xv. 2159.
[3] Lipp, *ibid.* xvi. 1290.
[4] Erlenmeyer and Rosenhek, *ibid.* xix. 2464.
[5] Baeyer, *ibid.* xiii. 2262.
[6] Lipp, *ibid.* 2649.
[7] Lipp, *Ber. Deutsch. Chem. Ges.* xix. 2643.

Atroglyceric acid, $C_6H_5.C(OH)(CH_2.OH)CO_2H$, is formed, together with acetophenone, when *a*-phenyldibromopropionic acid is treated in the cold with sodium carbonate solution [1] or when its nitril is decomposed with hydrochloric acid.[2] It separates from hot water in small needles, united to warty aggregates, melting at 146°.

Atroglyceronitril, $C_6H_5.C(OH)(CH_2.OH)CN$, is formed by the combination of benzoylmethyl alcohol, $C_6H_5.CO.CH_2.OH$, with hydrocyanic acid, and crystallizes from ether in long, thick needles.

a-Phenyldibromopropionic acid or *Dibromohydratropic acid*, $C_6H_5.CBr(CH_2Br)CO_2H$, is obtained by adding bromine to atropic acid in solution in carbon disulphide, from which it separates in long, silky needles, while it crystallizes from hot chloroform in small, pointed needles, united to druses, which melt at 115°—116°. On boiling with water it decomposes into carbon dioxide, hydrobromic acid and acetophenone.[3] The formation of the latter is analogous to that of phenylacetaldehyde from phenylbromolactic acid, the first product being the alcohol, $C_6H_5.C(OH)=CH_2$, which then passes into the ketone.[4]

PHENYLPROPYLENE $C_6H_5.CH=CH.CH_3$.

2381 This hydrocarbon, which is also termed *allylbenzene*, is formed in small quantity, together with phenylpropyl alcohol, by the action of sodium amalgam and hot water on cinnyl alcohol,[5] $C_6H_5.CH=CH.CH_2.OH$, and also, together with toluene and probably ethyl iodide, when the alcohol is heated to 180°—200° with hydriodic acid:

$$(1)\ C_6H_5.CH=CH.CH_2.OH + 2HI = C_6H_5.CH=CH.CH_3 + H_2O + I_2$$

$$(2)\ C_6H_5.CH=CH.CH_3 + 3HI = C_6H_5.CH_3 + CH_3.CH_2I + I_2.$$

[1] Fittig and Kast, *Ann. Chem. Pharm.* ccvi. 29.
[2] Plöchl and Blümlein, *Ber. Deutsch. Chem. Ges.* xvi. 1290.
[3] Fittig and Wurster, *Ann. Chem. Pharm.* cxcv. 159.
[4] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xiii. 309.
[5] Fittig and Krügener, *ibid.* vi. 214; Rügheimer, *Ann. Chem. Pharm.* clxxii. 122.

Phenylpropylene may also be obtained by heating phenylcrotonic acid, $C_6H_5.CH{=}C(CH_3)CO_2H$, or better by combining it with hydrobromic acid and decomposing the product with carbonate of soda.[1] It is also formed by the distillation of secondary phenylpropyl bromide,[2] by the action of alcoholic potash on secondary phenylpropyl chloride[3] and by the treatment of ethylphenylcarbinol with phosphorus pentachloride.[4]

It is a strongly refractive, pleasant-smelling liquid, which boils at 174°—175° and has a sp. gr. of 0·9180 at 15°. On boiling with sodium it passes into a polymeric modification, which boils above 330° and probably corresponds to distyrolene (Errera). Chojnacki, by heating benzene with zinc dust and allyliodide, obtained an isomeric hydrocarbon, which boils at 155°[5] and is probably the true allylbenzene, $C_6H_5.CH_2.CH{=}CH_2$.

Phenylpropylene bromide, $C_6H_5.CHBr.CHBr.CH_3$, is formed by the combination of the hydrocarbon with bromine,[6] and has also been obtained from propylbenzene (p. 153). It crystallizes from alcohol in long needles, melting at 66·5°.

Phenylnitropropylene, $C_6H_5.CH{=}C(NO_2)CH_3$, is obtained, accompanied by resinous products and benzamide, when benzaldehyde is heated to 130°—140° with nitroethane and zinc chloride. It crystallizes from petroleum-spirit in yellow, lustrous needles or transparent prisms, which melt at 64° and volatilize readily in steam; the vapour smells like nutmeg. It combines with bromine to form the dibromide, $C_6H_5.CHBr.CBr(NO_2)CH_3$, which crystallizes in transparent lustrous prisms, melting at 77°—78·5°. It is converted by fuming nitric acid into the following compounds, which can readily be separated by means of alcohol.

Orthonitrophenylnitropylene, $C_6H_4(NO_2)CH{=}C(NO_2)CH_3$, is readily soluble in alcohol and crystallizes in light yellow plates, melting at 76°—77.° It yields orthonitrobenzoic acid on oxidation.

Paranitrophenylnitropropylene forms yellow needles, which are only slightly soluble in alcohol, melt at 114°—115° and are oxidized to paranitrobenzoic acid by potassium permanganate.[7]

[1] Tiemann, *Ber. Deutsch. Chem. Ges.* xi. 617.
[2] Perkin, *Journ. Chem. Soc.* 1877, ii. 660.
[3] Radziszewski, *Jahresber. Chem.* 1874, 393.
[4] Errera, *Ber. Deutsch. Chem. Ges.* xviii. Ref. 149.
[5] *Compt. Rend.* lxxvi. 1413.
[6] Rügheimer, Radziszewski, Perkin, *loc. cit.*
[7] Priebs, *Ann. Chem. Pharm.* ccxxv. 319.

2382 *Anol* or *Allylphenol*, $C_3H_5.C_6H_4.OH$, was first prepared by Ladenburg by heating its methyl ether or anethol to 200°—230° with caustic potash. It crystallizes in small plates, which melt at 93°, become yellow in the air and then change into a brown oil. This alteration takes place partially on distillation, even in an atmosphere of carbon dioxide, and also on heating with dilute acids. A portion of the phenol is always oxidized to parahydroxybenzoic acid during its preparation.[1]

Anethol, $C_3H_5.C_6H_4(OCH_3)$, occurs, accompanied by a larger or smaller quantity of a terpene, $C_{10}H_{16}$, in the essential oil of the seeds of *Anethum foeniculum*, *Pimpinella anisum*, *Artemisia dracunculus*, and *Illicium anisatum*, and is deposited in plates when these oils are cooled.[2] Perkin, who names it *parallylanisoïl*, obtained it by heating methylparahydroxyphenylcrotonic acid.[3]

$$C_6H_4\begin{cases}OCH_3\\CH{=}CH.CH_2.CO_2H\end{cases} = C_6H_4\begin{cases}OCH_3\\CH{=}CH.CH_3\end{cases} + CO_2.$$

It has a more pleasant but fainter odour than oil of anise, melts at 21°, boils at 232° and has a sp. gr. of 0·989 at 28°. On boiling with hydriodic acid it yields methyl iodide, while the anol, which is simultaneously formed, is converted into a resinous mass.[4] It is oxidized by chromic acid solution to anisic acid and acetic acid. On heating with phosphorous chloride, *chloranethol*, $C_6H_4(OCH_3)C_3H_4Cl$, is formed. This substance boils at 258°, and on boiling for some time with alcoholic potash is converted into *allylenephenyl methyl ether*, $C_6H_4(OCH_3)C{\equiv}C.CH_3$, which is a liquid, boiling at 240° and possessing a faint but pleasant odour (Ladenburg).

Anethol readily forms polymeric modifications.

Metanethol, $(C_{10}H_{12}O)n$, is formed by heating anethol with zinc chloride,[5] and crystallizes from glacial acetic acid or ether in very thin needles, which melt at 132°. It commences to sublime at 115°, is volatile in superheated steam and boils with decomposition above 300°. It is attacked by bromine with evolution of hydrobromic acid.[6]

[1] *Ann. Chem. Pharm.* Suppl. viii. 87.
[2] Cahours, *ibid.* xli. 75; Laurent, *ibid.* xliv. 313; Gerhardt, *ibid.* xliv. 318; lii. 401.
[3] *Journ. Chem. Soc.* 1877, ii. 669.
[4] Ladenburg and Leverkus, *Ann. Chem. Pharm.* cxli. 260.
[5] Gerhardt, *Journ. Prakt. Chem.* xxxvi. 167.
[6] Perrenond, *Ann. Chem. Pharm.* clxxxvii. 63.

Anisoïn, $(C_{10}H_{12}O)n$, is obtained by the action of sulphuric acid or phosphoric acid (Cahours), antimony trichloride, tetrachloride (Gerhardt), benzoyl chloride[1] or a solution of iodine in potassium iodide[2] on anethol. It crystallizes from ether in small needles, which melt at 140°—145°. It is resolved by distillation into *isanethol* and *volatile metanethol*, the latter being a liquid, which boils at 232·5° and has a sp. gr. of 0·9706 at 18°. It is converted into anisoïn by sulphuric acid.

Isanethol is a thick, yellowish liquid, which remains unaltered at 380° and is converted into anisoïn by agitation with sulphuric acid.[3]

2383 *Eugenol*, $CH_3O.C_6H_3(OH)C_3H_5$, forms the chief constituent of the essential oil of cloves (*Eugenia caryophyllata*), of allspice (*Eugenia pimenta*),[4] of the leaves of the cinnamon tree (*Cinnamomum zeylanicum*),[5] of canella bark (*Canella alba*),[6] and probably of the Brazilian cinnamon (*Dycipellium caryophyllatum*),[7] and also occurs in that of the leaves of *Illicium religiosum*.

Bonastre found that oils of cloves and allspice form crystalline compounds with bases, and Dumas then analysed the first of these and obtained the formula $C_{40}H_{52}O_5$.[8] Liebig and Etling, however, found that it is a mixture of a terpene, $C_{10}H_{16}$, with a substance which combines with bases and was called by them *eugenic acid* (Nelkensäure).[9] This substance, was subsequently recognized as a phenol. Eugenol is also formed by the action of sodium amalgam and water on coniferyl alcohol[10] (p. 205).

In order to separate it from oil of cloves, three parts of this are shaken up with a solution of one part of caustic potash in ten parts of water, the insoluble terpene removed and the eugenol liberated from the alkaline solution by hydrochloric acid, washed with water and rectified.[11] It is a strongly refractive liquid, which becomes brown in the air, has the characteristic

[1] Kraut and Uelsmann, *Journ. Prakt. Chem.* lxxvii. 490.
[2] Rhodius, *Ann. Chem. Pharm.* lxv. 230.
[3] Kraut and Schlun, *Jahresb. Chem.* 1863, 552.
[4] Bonastre, *Ann. Chim. Phys.* xxxv. 274.
[5] Stenhouse, *Ann. Chem. Pharm.* xcv. 103; Schaer, *Ber. Deutsch. Chem. Ges.* xv. 2624.
[6] Wöhler, *ibid.* xlvii. 234.
[7] *Gmelin's, Organ. Chem.* iv. 200.
[8] *Ann. Chem. Pharm.* ix. 65.
[9] *Ibid.* ix. 68.
[10] Tiemann, *Ber. Deutsch. Chem. Ges.* ix. 418.
[11] Erlenmeyer, *Zeitschr. Chem.* 1866, 430; Wassermann, *Ann. Chem. Pharm.* clxxix. 369.

smell and burning taste of cloves, boils with slight decomposition at 247·5° and has a sp. gr. of 1·0799 at 0°, and of 1·063 at 18°. It is a stronger antiseptic than phenol, and can be taken in small doses to the extent of 3 grms. in twelve hours without producing noteworthy effects. Larger quantities cause giddiness and headache. It is found in the urine as eugenolsulphuric acid, which readily decomposes with liberation of eugenol.[1]

The alcohol solution is coloured blue by ferric chloride; it reduces ammoniacal silver solution, but not Fehling's solution, and when brought in contact with dry silver oxide ignites and burns brilliantly.[2] Nitric acid oxidizes it to oxalic acid, while acetic acid and carbon dioxide are formed by the action of chromic acid,[3] and it is converted into vanillin by potassium permanganate.[4] On fusion with caustic potash, it yields protocatechuic acid,[5] and is converted into a resin by heating with hydriodic acid, methyl iodide being also formed.[6]

Its salts have been investigated by Bonastre, von Brüning,[7] and Williams.[8]

Methyleugenol, $C_3H_5.C_6H_3(OCH_3)_2$, is formed by the action of methyl iodide on sodium eugenate,[9] and is a liquid, which boils at 244°—245°[10] and is oxidized to dimethylprotocatechuic acid by potassium dichromate and glacial acetic acid.

Ethyleugenol, $C_3H_5.C_6H_3(OCH_3)OC_2H_5$, is prepared by heating eugenol with ethyl bromide and caustic potash solution.[11] It is an aromatic liquid, which possesses a faint smell of cloves, is strongly refractive, boils at 254° and is partially converted by distillation into a polymeric modification, which crystallizes from alcohol in plates, melting at 125° and subliming at a higher temperature. It is oxidized by chromic acid to methylethylprotocatechuic acid and acetic acid.

Cahours has also prepared the following ethers:[12]

[1] De Regibus, *Ber. Deutsch. Chem. Ges.* xx. Ref. 435.
[2] Böttger, *Journ. Prakt. Chem.* lxxvi. 241.
[3] Wassermann, *Ann. Chem. Pharm.* clxxix. 372.
[4] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* ix. 273.
[5] Hlasiwetz and Grabowsky, *Ann. Chem. Pharm.* cxxxix. 96.
[6] Erlenmeyer, *Zeitschr. Chem.* 1866, 430.
[7] *Ann. Chem. Pharm.* civ. 204.
[8] *Ibid.* cvii. 241.
[9] Gräbe and Borgmann, *ibid.* clviii. 282.
[10] Matsmoto, *Ber. Deutsch. Chem. Ges.* xi. 123.
[11] Cahours, *Compt. Rend.* xlvi. 220; Wassermann, *Ann. Chem. Pharm.* clxxix. 375.
[12] *Ber. Deutsch. Chem. Ges.* x. 237; *Jahresb. Chem.* 1877, 580.

	Boiling-point.
Isopropyleugenol, $C_9H_8(OCH_3)OCH(CH_3)_2$ . .	252°—254°
Propyleugenol, $C_9H_8(OCH_3)OC_3H_7$	263°—265°
Isobutyleugenol, $C_9H_8(OCH_3)OC_4H_9$	272°—274°
Amyleugenol, $C_9H_8(OCH_3)OC_5H_{11}$	283°—285°
Hexyleugenol, $C_9H_8(OCH_3)OC_6H_{13}$	296°—300°
Allyleugenol, $C_9H_8(OCH_3)OC_3H_5$	267°—270°

	Melting-point.
Ethylene-eugenol, $(CH_3OC_9H_8O)_2C_2H_4$, prisms	89°
Propylene-eugenol, $(CH_3OC_9H_8O)_2C_2H_3.CH_3$, needles	56°—58°
Trimethylene-eugenol, $(CH_3OC_9H_8O)_2C_3H_6$, rhomb. prisms	82·5°

Acetyleugenol, $C_9H_8(OCH_3)O.CO.CH_3$, is formed when eugenol is boiled with acetic anhydride, and is a crystalline mass, which melts at 30°—31°, boils at 270° and is oxidized by potassium permanganate to acetalphahomovanillic acid (p. 25).[1]

Benzoyleugenol, $C_9H_8(OCH_3)O.CO.C_6H_5$, is obtained by heating eugenol with benzoyl chloride,[2] and crystallizes on the gradual evaporation of its alcoholic solution in large, transparent, vitreous, monosymmetric prisms, melting at 69°—70°. Chromic acid oxidizes it to benzoylvanillic acid.[3]

Eugenolglycolic acid, $C_9H_6(OCH_3)OCH_2.CO_2H$, is prepared by the evaporation of a mixture of eugenol, chloracetic acid and caustic soda solution, and crystallizes from hot water in long, silky needles, which melt at 80°—81°.[4]

Iso-eugenol, $CH_3O.C_6H_3(OH)C_3H_5$, is formed when homoferuläic acid, $C_9H_7(OH)(OCH_3)CO_2H$, is heated in a current of carbon dioxide, and is a strongly refractive liquid, the smell of which resembles that of eugenol, but can easily be distinguished from it. It boils at 258°—262°, and has a sp. gr. of 1·080 at 16°; its alcoholic solution is coloured light green by ferric chloride.

Benzoyliso-eugenol forms crystals, which melt at 159°—160°.[5]

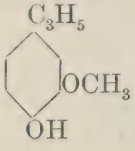
2384 *Meta-eugenol* or *Allylresorcinol methyl ether* is obtained by carefully heating methyl-β-methylumbellic acid, $C_6H_3(OH)(OCH_3)C(CH_3)=CH.CO_2H$, and is a thick, pleasant-smelling

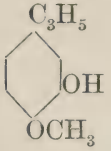
[1] Nagai and Tiemann, *Ber. Deutsch. Chem. Ges.* x. 201.
[2] Cahours, *Ann. Chem. Pharm.* cviii. 321.
[3] Tiemann and Kraaz, *Ber. Deutsch. Chem. Ges.* xv. 2067.
[4] Saarbach, *Journ. Prakt. Chem.* [2], xxi. 158.
[5] Tiemann and Kraaz, *Ber. Deutsch. Chem. Ges.* xv. 2064.

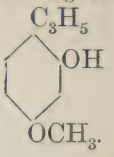
liquid, which boils at 245°—250° and dissolves in caustic soda but not in sodium carbonate solution.[1]

The constitutions of the phenol ethers here described are shown by the following formulæ:

Anethol.

Eugenol. 

Iso-eugenol. 

Meta-eugenol. 

Olivil, $C_{14}H_{18}O_5$, is the crystalline constituent of the resin of the wild olive (Part IV. p. 314), and forms a thick vapour on heating and has a pleasant odour resembling those of benzoïn and cloves, which is employed in Italy for the fumigation of sick rooms. In order to obtain the olivil, the resin is extracted with ether and the residue treated with boiling alcohol. The olivil, which separates on cooling, is washed with cold dilute alcohol and recrystallized from alcohol. It forms white needles, which are odourless and have a sweetish, bitter taste, melt at 120° and solidify to an amorphous mass, which forms a strongly-electrified powder on trituration. This mass melts at 70°, but after recrystallization from alcohol regains the original melting-point. It crystallizes from hot water in stellate groups of prisms, which contain one molecule of water. It is readily soluble in alkalis and precipitates the metals from solutions of gold chloride and silver nitrate. On dry distillation it yields an oily liquid, to which Sobrero has given the name of *pyro-olivilic acid*.[2] It has the composition and properties of eugenol and is either identical with this or iso-eugenol. When olivil is heated with hydriodic acid, a carbonaceous mass is formed and a mixture of methyl and ethyl iodides distils over.[3] The latter is undoubtedly a decomposition product of the allyl group, so that olivil must be looked upon as eugenol in which one hydrogen atom has been replaced by the group $C_4H_7O_3$, the constitution of which has not yet been determined.

2385 *Safrol*, $C_{10}H_{10}O_2$, is the chief constituent of sassafras-oil,[4] which is contained in the root of the American cinnamon tree (*Sassafras officinalis*), and is extracted in the United States

[1] Pechmann and Cohen, *ibid.* xvii. 2132.
[2] *Ann. Chem. Pharm.* liv. 67.
[3] Amato, *Ber. Deutsch. Chem. Ges.* xi. 1251.
[4] St. Evre, *Ann. Chem. Pharm.* lii. 396.

by distillation with water. This oil contains 90 per cent. of safrol, about 10 per cent. of safrene, $C_{10}H_{16}$, and a very small amount of a phenol, which gives a bluish green colouration with ferric chloride.[1] Safrol also occurs in the oil of the camphor tree and is identical with *shikomol*, which occurs, together with eugenol and *shikimene*, $C_{10}H_{16}$, which is probably safrene, in the ethereal oil of the leaves of the Japanese star anise (*Illicium religiosum*) or *shikimino-ki*.[2]

In order to obtain it pure, the fraction of sassafras-oil, which boils between 228°—235°, is cooled to − 25°, at which temperature the safrol is deposited in strongly refractive, mono-symmetric crystals,[3] melting at + 8°. It has a pleasant aromatic odour, boils at 232°, is insoluble in alkalis and is not attacked by sodium.

Tournefort discovered in 1698 that oil of sassafras is ignited by fuming nitric acid, and safrol itself has been found to detonate violently with the concentrated acid. If safrol, however, be heated with the dilute acid, it takes a red colour, which was observed by Bonastre, and a red-coloured resin is deposited, oxalic acid being also formed.[4] It is oxidized by a dilute solution of potassium permanganate to carbon dioxide, formic acid, propionic acid and piperonylic acid (Pt. IV. p. 355).[5] It is therefore, like anethol and eugenol, a derivative of allylbenzene:

Anethol. $C_6H_4(OCH_3)(C_3H_5)$

Eugenol. $C_6H_3(OH)(OCH_3)(C_3H_5)$

Safrol. $C_6H_3(O_2CH_2)(C_3H_5)$

It is worthy of note that the fruit of *Illicium anisatum* contains anethol, while eugenol and safrol occur in the leaves of *Illicium religiosum*, and are also found in various members of the allied family of Lauraceae; again, the root of the American cinnamon and the wood of the camphor tree contain safrol, while the leaves of the true cinnamon contain eugenol.

The fruits of *Illicium religiosum* and *I. anisatum* also contain protocatechuic acid and *shikiminic acid*, $C_7H_{10}O_5$, which is a crystalline powder, melting at 178°—180°. It is monobasic, is converted into protocatechuic acid by fusion with potash and

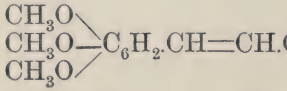
[1] Grimaux and Ruotte, *ibid.* clii. 88; Flückiger and Hanbury, *Pharmacographia*, 2nd Ed. 538.
[2] Eijkmann, *Recueil Trav. Chim. Pays-Bas.* iv. 32.
[3] Arzruni, *Jahresbr. Chem.* 1876, 910.
[4] J. Schiff, *Ber. Deutsch. Chem. Ges.* xvii. 1935.
[5] Eijkmann, *loc. cit.*; Poleck, *Ber. Deutsch. Chem. Ges.* xix. 1094.

yields ordinary phenol on the distillation of its calcium salt. It appears therefore to be a *tetrahydrotrihydroxybenzoic acid*,[1] $C_6H_6(OH)_3CO_2H$.

2383 *Asaron*, $C_{12}H_{16}O_3$, was discovered in 1814 by Görz in the root of Asarabacca (*Asarum europaeum*), and obtained by the distillation of the root with water. He gave it the name of Asarabacca-camphor, and noticed that it had a sharp, camphor-like smell and taste and acted as an emetic. Subsequent investigations have shown that these properties are due to the admixture of an ethereal oil. Asaron was analysed by Blanchet and Sell,[2] and afterwards by Schmidt,[3] who also investigated it crystallographically; its correct formula was however first given by Rizza and Butlerow, who determined its vapour density and were thus enabled to ascertain its constitution.[4]

Asaron crystallizes in various combinations of the monosymmetric system, is odourless, has a faintly biting taste, melts at 59°, boils at 296° and can be distilled in small quantities without undergoing decomposition. It dissolves readily in alcohol, ether, &c., and also to some extent in hot water, from which it crystallizes in delicate needles and small plates. It unites with bromine to form the crystalline compound, $C_{12}H_{16}Br_2O_3$.

On oxidation it yields the aldehyde, $C_{10}H_{12}O_4$, as the first product, accompanied by acetic acid, oxalic acid and carbon dioxide. It forms long, silky crystals and melts at 114°. The acid, $C_{10}H_{12}O_5$, which is derived from this, crystallizes in needles, melts at 143° and boils at about 300°. Neither of these substances behave as unsaturated compounds; if they or asaron itself be heated with hydriodic acid, methyl iodide is formed in considerable quantity, and when the acid is distilled with slaked lime, an oily liquid, $C_9H_{10}O_3$, is obtained, which boils at 245°—248°, and gives three molecules of methyl iodide when heated for a long time with hydriodic acid, from which it follows that it is the methyl ether of trihydroxybenzene. The acid is therefore a trimethoxybenzoic acid, $(CH_3O)_3C_6H_2CO_2H$, and asaron has probably the following constitution:



[1] Eijkmann, *Ber. Deutsch. Chem. Ges.* xviii. Ref. 281; xx. Ref. 67.
[2] *Ann. Chem. Pharm.* vi. 297. [3] *Ibid.* liii. 156.
[4] *Ber. Deutsch. Chem. Ges.* xvii. 1159; xx. Ref. 222.

According to this view the acid stands in the same relation to asaron as veratric acid to methyleugenol or anisic acid to anethol.

PHENYLALLYL COMPOUNDS.

2387 *Phenylallyl alcohol*, $C_6H_5.CH{=}CH-CH_2.OH$. Simon found in 1839 that the styracin, which was discovered by Bonastre in liquid styrax (p. 27), is converted by boiling with caustic soda solution into cinnamic acid and an oily liquid, which he named *styraçone*.[1] Toel repeated these researches, making use of purified styracin, and instead of a liquid obtained a crystalline substance, which he named *styrone*, assuming that styracin is a compound of similar constitution to the fats and consists of cinnamic acid and *styryl oxide*, the latter of which combines with water on saponification to form styrone, just as glycerin is formed from lipyl oxide (Pt. II. p. 344).[2] Strecker determined the correct formula of styrone and showed that it stands in the same relation to cinnamic acid as alcohol to acetic acid, in other words that it is the alcohol of cinnamic acid.[3] This was confirmed by Wolff, who converted it into the latter by oxidation.[4]

Further investigations have shown that cinnamyl alcohol, which is also called cinnyl or styryl alcohol,[5] is phenylallyl alcohol, and that Simon's styraçone was a mixture of this with phenylpropyl alcohol.[6]

Cinnyl alcohol occurs, probably as cinnamate, in Peru balsam (Pt. IV. p. 90).[7]

In order to prepare it, styrax is distilled with sodium carbonate solution until styrolene no longer passes over, the aqueous solution containing sodium cinnamate removed, the residue distilled with caustic potash and the cinnyl alcohol separated from phenylpropyl alcohol by the fractional distillation of the oily distillate. Pure styracin may also be distilled with caustic potash; the cinnyl alcohol crystallizes out of the distillate, while

[1] *Ann. Chem. Pharm.* xxxi. 265.
[2] *Ibid.* lxx. 1. [3] *Ibid.* lxx. 11. [4] *Ibid.* lxxv. 297.
[5] The name styryl alcohol is liable to be confused with styrolyl alcohol (p. 6), and since the radical of cinnamic acid is designated cinnamyl, it is most convenient to employ the name cinnyl alcohol, which was proposed by Henry Watts.
[6] Rügheimer, *Ann. Chem. Pharm.* cvxxii. 22; V. Miller, *ibid.* cxxxviii. 184.
[7] Delafontaine, *Zeitschr. Chem.* 1869, 156.

any remaining in the solution is precipitated with salt or extracted with ether.

Cinnyl alcohol crystallizes in long, thin needles, which melt at 33°, and have a pleasant smell of hyacinths; it boils at 250, is tolerably soluble in water, readily in alcohol and ether and is oxidized to cinnamaldehyde by platinum black.[1] It is converted into phenylpropyl alcohol by the action of sodium amalgam on its warm aqueous solution, a little allylbenzene being simultaneously formed. If, however, an amalgam containing 15 per cent. of sodium be employed with only a little water, the mixture being heated on the water-bath, it is resolved into styrolene and methyl alcohol:[2]

$$C_6H_5.CH{=}CH.CH_2.OH + 2H = C_6H_5.CH{=}CH_2 + CH_3.OH.$$

On heating to 180°—200° with concentrated hydriodic acid, it is reduced to allylbenzene; toluene is formed at the same time, the amount increasing with the duration of the experiment, and ethyl iodide is also probably among the products (see p. 194).[3]

Cinnyl alcohol combines with bromine to phenyldibromopropyl alcohol or styceryl dihydrobromide, $C_6H_5.CHBr.CHBr.CH_2.OH$.

The following cinnyl compounds have been investigated by Ramdohr.[4]

Cinnyl ethyl ether, $C_6H_5.C_3H_4.O.C_2H_5$, is a heavy liquid, which boils at a high temperature.

Dicinnyl ether, $(C_6H_5.C_3H_4)_2O$, is formed when the alcohol is heated with boron trioxide, and is a thick, oily liquid, which has an odour resembling that of cinnamon and partially decomposes on distillation.

Cinnyl chloride, $C_6H_5.C_3H_4Cl$, is a yellowish, oily liquid, the smell of which resembles those of oil of anise and oil of cinnamon; it decomposes on distillation even under diminished pressure.

Cinnyl iodide, $C_6H_5.C_3H_4I$, is a heavy, aromatic-smelling liquid, which has a burning taste and decomposes even on distillation with water.

Cinnylamine, $C_6H_5.C_3H_4.NH_2$, forms small, colourless crystals, which have a very bitter taste and readily fuse to an oil, which volatilizes even at 100°, forming a vapour which has an alkaline reaction.

[1] Strecker, *Ann. Chem. Pharm.* xciii. 370.
[2] Hatton and Hodgkinson, *Journ. Chem. Soc.* 1881, i. 319.
[3] Tiemann, *Ber. Deutsch. Chem. Ges.* xi. 671.
[4] *Jahresber. Chem.* 1858, 446.

2388 *Coniferyl alcohol*, $CH_3O.C_6H_3(OH)CH{=}CH.CH_2.OH$, is obtained by the action of emulsion on its glucoside, coniferin, suspended in 10 parts of water. The mixture is allowed to stand for 6—8 days at 25°—36°, and the whole repeatedly extracted with ether. The residue after the evaporation of the ether is then purified by recrystallization from ether.

Coniferyl alcohol crystallizes in prisms, which melt at 74°, are scarcely soluble in cold, only slightly in hot water and more readily in alcohol. It is immediately polymerized by dilute acids to an amorphous substance, which is less soluble in alcohol and ether and softens at 150°—160°. Chromic acid oxidizes coniferyl alcohol to vanillin and acetaldehyde ; it yields protocatechuic acid on fusion with potash, and is reduced to eugenol by the action of sodium amalgam and water. As a phenol it forms crystalline compounds with the alkalis. On heating with hydriodic acid, methyl iodide, ethyl iodide and bromocatechol are formed, accompanied by a resinous mass :

$$C_6H_3\begin{cases}OH\\CH{=}CH.CH_2.OH\\OCH_3\end{cases} + 4HI =$$

$$C_6H_3\begin{cases}OH\\CH_3\\OH\end{cases} + CH_3I + CH_3.CH_2I + I_2 + H_2O.$$

This decomposition corresponds to that which cinnyl alcohol undergoes when heated with hydriodic acid.[1]

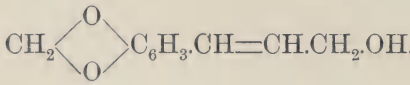
Coniferin, $CH_3O.C_6H_3(C_3H_4.OH)O.C_6H_{11}O_5 + 2H_2O$, occurs in the cambium sap of the coniferæ.[2] Its preparation has already been described (see vanillin, Pt. IV. p. 345). It is slightly soluble in cold, more readily in hot water and alcohol, but is insoluble in ether, and crystallizes in stellate or rosette-shaped groups of pointed needles, which become anhydrous at 100° and melt at 185°. Its solution has a faintly bitter taste and is laevoorotatory. It forms a red solution in concentrated sulphuric acid, which deposits an indigo-blue resin on the addition of water. If it be moistened with phenol and concentrated sulphuric acid, it rapidly becomes coloured a deep blue, the change being almost instantaneous in the sunlight. Pine wood can thus be employed to detect phenol, or the presence of

[1] Tiemann and Haarmann, *Ber. Deutsch. Chem. Ges.* vii. 608 ; viii. 1127 ; xi. 667.

[2] Hartig and Kubel, *Zeitschr. Chem.* 1866, 339.

coniferin may be ascertained in the various pines, which contain it both when fresh and after being preserved for a considerable period.

2389 *Cubebin*, $C_{10}H_{10}O_3$, occurs in cubebs,[1] which are the unripe fruits of *Piper Cubeba*, and separates from their ethereal extract when this is preserved for some time.[2] In order to prepare it, the powdered cubebs are freed from ethereal oil by distillation with water and are then extracted with boiling alcohol, the solvent distilled off and the solution purified by recrystallization.[3] It forms tasteless and odourless needles, which are scarcely soluble in water and melt at 125°.[4] On heating with caustic potash it is decomposed into protocatechuic acid, acetic acid and carbon dioxide, and it is oxidized by alkaline permanganate solution to piperonylic acid,[5] so that it has the following constitution :



Nitrocubebin, $C_{10}H_9(NO_2)O_3$, was obtained by Weidel by the action of nitrogen dioxide on an ethereal solution of cubebin ; it crystallizes in light yellow needles, which form a purple-violet solution in caustic potash.

PHENYLACRYL-COMPOUNDS.

Cinnamaldehyde, $C_6H_5.CH{=}CH.CHO$.

2390 Cinnamon (*Cinnamomum zeylanicum*) and cassia bark or bastard-cinnamon, which is derived from various species of Cinnamomum growing in China and the Indies and are mentioned in the Pentateuch and by Herodotus and other authors, were considered as the most valuable of spices and were eagerly sought after by the earliest travellers in the East. The essential oils which are contained in them and in cloves, were first prepared

[1] Souberan and Capitaine, *Ann. Chem. Pharm.* xxxi. 190 ; Schmidt, *Ber. Deutsch. Chem. Ges.* x. 190.
[2] Schuck, *Rep. Pharm.* [2], i. 213 ; Engelhardt, *ibid.* iii. 1.
[3] Steer, *Ann. Chem. Pharm.* xxxvi. 331.
[4] Weidel, *Wien. Akad. Ber.* lxxiv. 377.
[5] Pomeranz, *Monatsh. Chem.* viii. 466.

in the middle of the sixteenth century by Valerus Cordus, who stated that these belong to the few essential oils, which are heavier than water.[1]

Trommsdorff observed in 1780 that water which has been distilled over cinnamon deposits a crystalline salt on standing, while other chemists found that crystals gradually separate out of oil of cinnamon, and these were mistaken for benzoic acid until Dumas and Peligot, in 1834, observed that they are a new acid, which they named cinnamic acid (*acide cinnamique*). They also found that oil of cinnamon bears the same relation to it as oil of bitter almonds or benzoyl hydride to benzoic acid, and therefore gave it the name of cinnamyl hydride (*hydrure de cinnamyle*).[2] It also occurs in the essential oil of the so-called flowers of cinnamon,[3] the unripe fruits of bastard-cinnamon. It is remarkable that the leaves of the cinnamon tree contain eugenol, but no cinnamaldehyde (p. 197).

Cinnamaldehyde was first synthetically prepared by Chiozza, who had found that cinnamic acid decomposes into acetic and benzoic acids on fusion with potash, and therefore endeavoured "to prepare cinnamic acid or cinnamyl hydride inversely from the atomic groups contained in benzoic and acetic acids." To this end he saturated a mixture of acetaldehyde and benzaldehyde with hydrochloric acid and heated; oily drops separated out and on distillation he obtained cinnamaldehyde, preceded by a little unaltered benzaldehyde:[4]

$$C_6H_5.CHO + CH_3.CHO = C_6H_5.CH{=}CH.CHO + H_2O.$$

It may be very easily prepared by allowing a mixture of 10 parts of benzaldehyde, 15 parts of acetaldehyde, 900 parts of water and 10 parts of a 10 per cent. solution of caustic soda to stand for 8—10 days at a temperature of 30°, the whole being frequently agitated and finally extracted with ether.[5]

Piria obtained it by the distillation of a mixture of calcium cinnamate and calcium formate.[6]

Oil of cinnamon contains, in addition to cinnamaldehyde, a hydrocarbon, which is probably a terpene, $C_{10}H_{16}$; these may be

[1] Flückiger and Hanbury, *Pharmacographia*, 2nd Ed. 219.
[2] *Ann. Chem. Pharm.* xiv. 50; *Ann. Chim. Phys.* lvii. 305.
[3] Mulder, *Ann. Chem. Pharm.* xxxiv. 147.
[4] *Ann. Chem. Pharm.* xcvii. 350.
[5] Peine, *Ber. Deutsch. Chem. Ges.* xvii. 2117.
[6] *Ann. Chem. Pharm.* c. 104.

separated, as discovered by Dumas and Peligot,[1] by bringing the oil into contact with concentrated nitric acid, the compound $(C_9H_8O_2)_2N_2O_5$ being formed, which separates out in long, oblique, rhombic prisms or small plates, and is decomposed by water into nitric acid and the free aldehyde. This characteristic compound has probably the following constitution:

$$\begin{matrix} C_6H_5.C_3H_3\text{—}ONO_2 \\ \qquad\quad >O \\ C_6H_5.C_3H_3\text{—}ONO_2 \end{matrix}.$$

Bertagnini obtained pure cinnamaldehyde by agitating oil of cinnamon with 3 or 4 volumes of a concentrated solution of acid potassium sulphite; the compound $C_6H_5.C_2H_2.CH(OH)SO_3K$ separated in scales, which were dried, washed with alcohol, again dried and finally decomposed with dilute sulphuric acid.[2] According to Peine, an alcoholic solution of 50 parts of oil of cinnamon is agitated with 90 parts of a 50 per cent. solution of acid sodium sulphite, and the compound, after washing with alcohol, decomposed with sulphuric acid, 40 cb. cm. of this, diluted with an equal volume of water, being employed for every 100 cb. cm. of the sulphite solution. The aldehyde is then distilled with steam, the distillate extracted with ether and, after the evaporation of the ether, fractionated under diminished pressure.[3]

Cinnamaldehyde is a colourless, very pleasant smelling liquid, which decomposes on distillation at the ordinary pressure, but boils without alteration at 130° under a pressure of 30—40 mm. (Peine). When it is added to a solution of a salt of rosaniline, which has been decolourized by sulphurous acid, a deep yellow colouration is produced, which soon passes into violet-red.[4]

Hydrocinnamide or *Cinnamidenediamine*, $(C_6H_5.CH{=}CH.CH)_3N_2$, was prepared by Laurent by the action of ammonia on oil of cinnamon.[5] In order to prepare it, pure cinnamaldehyde is dissolved in 3—4 volumes of absolute alcohol and dry ammonia passed into the cooled solution. After twenty-four hours the crystalline paste is washed with dilute alcohol, dissolved in alcohol and treated with an excess of hydrochloric acid. The salt $C_{27}H_{24}N_2ClH + 3H_2O$ separates out and is

[1] *Ann. Chem. Pharm.* c. 104. ; Mulder, *loc. cit.*
[2] *Ibid.* lxxxv. 271.
[3] *Ber. Deutsch. Chem. Ges.* xvii. 2109.
[4] Schmidt, *Ber. Deutsch. Chem. Ges.* xiv. 1849.
[5] *Journ. Prakt. Chem.* [1], xxvii. 309.

then dissolved in an additional quantity of alcohol and precipitated in tabular crystals by the addition of ether. If ammonia be added to the hot alcoholic solution, hydrocinnamide crystallizes out on cooling in white needles, melting at 106°. It is also formed when aqueous ammonia is repeatedly agitated with an ethereal solution of cinnamaldehyde during several weeks (Peine).

Cinnamaldoxime, $C_6H_5.CH{=}CH.CH{=}NOH$, is formed by the action of hydroxylamine on the aldehyde, and crystallizes from hot water or benzene in very fine needles, melting at 134°—136°.[1]

Cinnamidene-aniline, $C_6H_5.CH{=}CH.CH{=}NC_6H_5$, is obtained by heating cinnamaldehyde with aniline. It crystallizes from hot alcohol in yellow plates, melting at 109°, and is converted into phenylquinoline, $C_{15}H_{11}N$, by heating with hydrochloric acid.[2]

Cinnamidenephenylhydrazone, $C_6H_5.CH{=}CH.CH{=}N.NHC_6H_5$, is formed when cinnamaldehyde and phenylhydrazone or their alcoholic solutions are mixed, and crystallizes in yellow needles or plates, melting at 166°.[3]

Bromocinnamaldehyde or *Phenylbromacrylaldehyde*, $C_6H_5.CBr{=}CH.CHO$. Cinnamaldehyde combines with bromine to form *phenyldibromopropionaldehyde*, $C_6H_5.CHBr.CHBr.CHO$, a crystalline substance, which has a characteristic odour and causes a flow of tears. It readily decomposes with formation of phenylbromacrylaldehyde, which crystallizes from alcohol in thick tablets and from ether in large, very lustrous, monosymmetric prisms, melting at 72°—73°. Its phenylhydrazone forms broad, lustrous plates which turn brown in the air, become dark coloured at 122° and melt at 129°—130°. It is converted into *α*-bromocinnamic acid by oxidation.[4]

2391 *Orthonitrocinnamaldehyde* or *Orthonitrophenylacrylaldehyde*, $C_6H_4(NO_2)CH{=}CH.CHO$, was first synthetically prepared by Baeyer and Drewsen from orthonitrobenzaldehyde ; this body combines with acetaldehyde to form the aldehyde of orthonitro-*β*-phenyl-lactic acid, which loses water on boiling with acetic anhydride :[5]

$$C_6H_4(NO_2)CH(OH)CH_2.CHO = C_6H_4(NO_2)CH{=}CH.CHO + H_2O.$$

[1] Bornemann, *Ber. Deutsch. Chem. Ges.* xix. 1512.
[2] Döbner and v. Miller, *ibid.* xvi. 1664 ; Peine, *ibid.* xvii. 2117.
[3] Fischer, *ibid.* xvii. 575 ; Peine, *loc. cit.*
[4] Zincke and v. Hagen, *Ber. Deutsch. Chem. Ges.* xvii. 1814.
[5] *Ibid.* xvi. 2205.

Orthonitrocinnamaldehyde is also formed, together with the para-compound, when 25 grms. of cinnamaldehyde are gradually run into a well stirred and well cooled mixture of 500 grms. of sulphuric acid and 20 grms. of saltpetre. On pouring into water, the nitrated aldehydes separate out in flakes. The mixture is recrystallized from hot alcohol and is then redissolved in boiling absolute alcohol and heated with an equal volume of acid sodium sulphite solution. The compound of the para-nitro-aldehyde partially separates out on cooling and is completely precipitated by adding salt and allowing the solution to stand for twenty-four hours. The liquid is then filtered, diluted with 10 volumes of water and the ortho-compound precipitated with concentrated sulphuric acid, the last traces being extracted with benzene.[1]

Orthonitrocinnamaldehyde crystallizes from hot alcohol in fine needles, which melt at 127° and are readily soluble in boiling water. Its hydrazone forms Bordeaux-red needles, melting at 157·5°.

Paranitrocinnamaldehyde was prepared by Göhring by boiling the aldehyde of paranitro-β-phenyl-lactic acid,[2] and is also obtained by the decomposition of its sodium sulphite compound. It crystallizes from alcohol or hot water in long needles, which melt at 141°—142°. Its phenylhydrazone forms orange-red crystals, melting at 180°—181° (Diehl and Einhorn).

Metanitrocinnamaldehyde is formed when 100 grms. of meta-nitrobenzaldehyde are dissolved in two litres of alcohol and treated with four litres of water, 35 grms. of acetaldehyde and 70 grms. of 10 per cent. caustic soda solution. The precipitate is filtered off after twelve hours, washed with ether and recrystallized from hot dilute alcohol. It is thus obtained in long, thin prisms, while it crystallizes from hot water in fine needles, melting at 116°. Its phenylhydrazone forms garnet-red tablets, melting at 160°.[3]

α-Nitrophenylbromacrylaldehyde, $C_6H_4(NO_2)CBr{=}CH.CHO$, is obtained together with the following compound by the nitration of phenylbromacrylaldehyde (Zincke and v. Hagen). The two isomerides are separated by recrystallization from a mixture of benzene and petroleum-spirit, in which the α-compound is the less soluble. It forms yellowish, foliaceous needles or more

[1] Diehl and Einhorn, *Ber. Deutsch. Chem. Ges.* xviii. 2235.
[2] *Ibid.* xviii. 371.
[3] Kinkelin, *ibid.* xviii. 483.

compact crystals, which melt at 136°. Its hydrazone is ruby-red and melts at 154°. Reducing agents convert the *α*-compound into a red base, the hydrochloride of which forms almost black crystals.

β-Nitrophenylbromacrylaldehyde crystallizes in long, yellowish, transparent needles, melting at 96°—97°. Its hydrazone forms golden-yellow plates, which melt with decomposition at 134°.

γ-Nitrophenylbromacrylaldehyde is prepared by the addition of bromine to metanitrocinnamaldehyde and decomposition of the product with hot sodium acetate solution. It crystallizes from alcohol in long, fine needles, melting at 90°, and its hydrazone forms golden-yellow plates, which melt at 120° (Kinkelin).

CINNAMIC ACID OR β-PHENYLACRYLIC ACID, $C_6H_5.CH{=}CH.CO_2H$.

2392 This acid was for a long period mistaken for benzoic acid, but after Dumas and Peligot had shown that a characteristic acid is formed by the oxidation of oil of cinnamon, it was found that the acid contained in liquid styrax,[1] Peru balsam[2] and Tolu balsam is also cinnamic acid.[3]

It occurs in styrax partly in the free state and partly as styracin or cinnyl cinnamate, while the balsams contain the free acids accompanied by the benzyl ether of cinnamic and benzoic acids.[4] Both these acids have also been found in Sumatra benzoin;[5] cinnamic acid also occurs, according to Eijkman, in the leaves of the Japanese garden plant *Enkyanthus japonicus*,[6] and has been found by Heckel and Schlagdenhauffen in *Globularia Alypum* and *Globularia vulgaris*.[7]

[1] Buchner, *Rep. Pharm.* lv. 210; Fremy, *Ann. Chem. Pharm.* xxx. 330; Plantamour, *ibid.* xxx. 341; Simon, *ibid.* xxxi. 265; Marchand, *Journ. Prakt. Chem.* xvi. 60.

[2] Delafontaine, *Zeitschr. Chem.* 1869, 156; Kraut, *Ber. Deutsch. Chem. Ges.* ii. 180.

[3] Simon; Fremy, *loc. cit.*; Deville, *Ann. Chem. Pharm.* xliv. 304; Kopp, *ibid.* lx. 269; Busse, *Ber. Deutsch. Chem. Ges.* ix. 830.

[4] Aschoff, *Jahresber. Chem.* 1861, 400.

[5] Kolbe and Lautemann, *Ann. Chem. Pharm.* cxix. 136.

[6] *Ber. Deutsch. Chem. Ges.* xx. Ref. 66.

[7] *Ann. Chim. Phys.* [5], xxviii. 67.

Bertagnini obtained it synthetically by heating benzaldehyde with acetyl chloride to 120°—130°:[1]

$$C_6H_5.CHO + CH_3.COCl = C_6H_5.CH{=}CHCOCl + H_2O = C_6H_5.CH{=}CH.CO.OH + HCl.$$

It is also formed when benzaldehyde and glacial acetic acid are heated together to 16° in presence of hydrochloric acid or zinc chloride.[2]

It may also be obtained, acccording to Swarts, by the action of carbon dioxide on a mixture of *a*-bromostyrolene, $C_6H_5CH{=}CHBr$, and sodium. Erlenmeyer, who repeated this experiment, only obtained a mixture of phenylpropiolic acid, $C_6H_5.C{\equiv}C.CO_2H$, and phenylpropionic acid. The first of these, which was then unknown, was probably mistaken by Swarts for cinnamic acid.[3]

Perkin has found that the acids of the cinnamic series may be synthetically prepared by heating benzaldehyde with the anhydride of a fatty acid and the anhydrous sodium salt of the fatty acid. In order to prepare cinnamic acid in this way, a mixture of 1 part of sodium acetate, 2 parts of benzaldehyde and 3 parts of acetic anhydride is boiled for a day or heated for five to six hours in a sealed tube at 180°. The product is boiled with water to volatilize any unaltered benzaldehyde, and the impure cinnamic acid, which crystallizes out on cooling, is washed and dissolved in hot sodium carbonate solution; the liquid is allowed to cool and is then filtered in order to remove an oily impurity, the cinnamic acid being precipitated with hydrochloric acid and finally crystallized from dilute alcohol.

The formation of the cinnamic acid may be expressed by the following equation:

$$2C_6H_5.CHO + \begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!\!>\!O = \begin{matrix} C_6H_5.CH{=}CH.CO \\ C_6H_5.CH{=}CH.CO \end{matrix}\!\!>\!O + 2H_2O.$$

According to this, cinnamic anhydride is formed and is then decomposed by the boiling with water. When acetic anhydride and benzaldehyde are heated together, however, no cinnamic acid is formed, benzidene diacetate, $C_6H_5CH(OCO.CH_3)_2$ (Pt. IV. p. 137), being in this case the product. What then is the function of the sodium acetate? Perkin has found that it can

[1] *Ann. Chem. Pharm.* c. 125.
[2] Schiff, *Ber. Deutsch. Chem. Ges.* iii. 412.
[3] *Ibid.* xvi. 152.

be replaced by butyrate or valerate without affecting the production of cinnamic acid; these salts therefore appear either to act merely as dehydrating agents or to bring about a decomposition of the benzidene diacetate which is first formed.[1]

Perkin succeeded in preparing the homologues of cinnamic acid by employing other anhydrides. Fittig on the other hand found that when benzaldehyde is heated with acetic anhydride and the sodium salt of a higher fatty acid, an acid is formed, which must be looked upon as a condensation product of this higher acid with benzaldehyde, and concludes from this that the anhydride has merely a dehydrating action and that the sodium salt enters into the reaction, cinnamic acid being therefore formed according to the following equation:[2]

$$C_6H_5.CHO + CH_3.CO_2Na = C_6H_5.CH{=}CH.CO_2Na + H_2O.$$

Since, however, the lower acids are stronger acids than their higher homologues, it appears more probable that the sodium salts of the latter are decomposed by the anhydrides of the lower acids, the final product being always a condensation product of benzaldehyde with the higher acid, whether this is originally present in the form of anhydride or sodium salt.[3]

Slocum and Fittig have now ascertained that when benzaldehyde is heated with acetic anhydride and sodium butyrate to 100°, phenylangelic acid is the only product, while cinnamic acid is also formed at a higher temperature. Fittig, therefore, maintains his view that the reaction takes place between the benzaldehyde and the sodium salt, while, on the other hand, Perkin has shown that isobutyric anhydride is formed when acetic anhydride and sodium isobutyrate are heated together. Fittig has also proved that in many cases an hydroxy-acid is first formed and is then converted into an acetyl derivative by the acetic anhydride. Phenyl-lactic acid would thus be the first product of the action of sodium acetate on benzaldehyde:

$$C_6H_5.CHO + CH_3.CO_2Na = C_6H_5.CH\begin{<}OH\\CH_2.CO_2Na\end{.}$$

This acid or its acetyl derivative, acetylphenyl-lactic acid, would then decompose at a higher temperature into cinnamic

[1] *Journ. Chem. Soc.* 1877, i. 838.
[2] *Ber. Deutsch. Chem. Ges.* xiv. 14.
[3] Tiemann and Kraaz, *ibid.* xv. 2061.

acid and water or acetic acid. Fittig and Slocum were unable to prove the formation of either of these acids, since they are converted into cinnamic acid at a temperature below that at which benzaldehyde acts upon sodium acetate.[1]

That they are actually formed at one stage of the reaction is proved by the fact, that when sodium isobutyrate is employed, phenylhydroxypivalic acid, $C_6H_5.CH(OH)C(CH_3)_2CO_2H$, which is incapable of simple conversion into cinnamic acid, is formed. The accuracy of this view is also confirmed by the following reaction. When benzaldehyde is heated with acetic anhydride, benzidene diacetate is formed, as has already been mentioned. If this be heated with sodium acetate, cinnamic acid is formed,[2] and can be even more readily obtained by heating benzidene chloride with sodium acetate,[3] the diacetate being however the first product, as is also the case in Perkin's reaction.

In order to explain the conversion of this substance into cinnamic acid, we must assume that in the presence of sodium acetate it passes into the metameric acetylphenyl-lactic acid, which immediately undergoes decomposition :[4]

$$C_6H_5.CH\begin{matrix}O.CO.CH_3\\O.CO.CH_3\end{matrix} = C_6H_5.CH\begin{matrix}O.CO.CH_3\\CH_2.CO.OH\end{matrix} =$$

$$C_6H_5.CH{=}CH.CO.OH + HO.CO.CH_3.$$

Cinnamic acid is also formed when benzaldehyde is heated to 140° with malonic acid :[5]

$$C_6H_5.CHO + CH_2(CO_2H)_2 =$$
$$C_6H_5.CH{=}CH.CO_2H + CO_2 + H_2O.$$

Cinnamic acid was formerly prepared from liquid styrax, but is now manufactured by the method discovered by Caro, which can also be used for the preparation of substituted cinnamic acids by the employment of substitution products of benzidene chloride.[6]

Properties.—Cinnamic acid dissolves in 3500 parts of water at 17°; it is much more readily soluble in boiling water and crystallizes from it in lustrous plates, while it separates from

[1] *Ann. Chem. Pharm.* ccxxvii. 48.
[2] C. König, *Ber. Deutsch. Chem. Ges.* xv. 266.
[3] H. Caro, Private communication.
[4] Perkin, *Journ. Chem. Soc.* 1886, i. 317.
[5] Michael, *Amer. Chem. Journ.* v. 205.
[6] *Ber. Deutsch. Chem. Ges.* xv. 969.

alcohol in monosymmetric prisms, melting at 133°.[1] It sublimes in a similar manner to benzoic acid but somewhat less readily, is volatile in steam and boils at 300°—304°, but partially decomposes on continued boiling into styrolene and carbon dioxide. It undergoes the same decomposition when heated with lime or baryta, benzene being also formed.[2] It also yields benzene in considerable quantity on fusion with caustic soda,[3] while it is resolved into benzoic and acetic acids when caustic potash is employed.[4] Oxidizing agents convert it first into benzaldehyde, so that it can in this way be readily distinguished from benzoic acid.[5] When taken internally it undergoes oxidation and appears in the urine as hippuric acid.[6] It is converted into hydrocinnamic acid by sodium amalgam and water.

2393 *The Cinnamates.* These salts, which resemble the benzoates, have been chiefly investigated by Herzog[7] and Kopp.[8] The salts of the alkali metals combine with cinnamic acid to form so-called acid salts.

Acid sodium cinnamate, $C_9H_7NaO_2 + C_9H_8O_2$, was prepared by Perkin by heating benzaldehyde in a sealed tube with acetic anhydride and sodium acetate. It forms a white, opaque mass and is decomposed by water into the normal salt and cinnamic acid.

Calcium cinnamate, $(C_9H_7O_2)_2Ca + 3H_2O$, crystallizes in needles, which dissolve in 608 parts of water at 17·5° (Kraut).

Barium cinnamate, $(C_9H_7O_2)_2Ba + 2H_2O$, is even less soluble than the calcium salt and crystallizes from hot water in plates.

The soluble salts give a yellow precipitate with ferric chloride. It may be distinguished from benzoic acid and atropic acid (p. 233) by the fact that its soluble normal salts give an immediate precipitate with manganese chloride.

Methyl cinnamate, $C_9H_7O_2(CH_3)$, forms crystals, which have a very pleasant odour, melt at 33·4° and boil at 263°.[9]

Ethyl cinnamate, $C_9H_7O_2(C_2H_5)$ is a pleasant smelling liquid, boiling at 271° (Anschütz and Kinnicutt), which is contained in liquid styrax.

[1] Kraut, *Ann. Chem. Pharm.* cxlvii. 112.
[2] Howard, *Jahresb. Chem.* 1860, 303.
[3] Barth and Schreder, *Ber. Deutsch. Chem. Ges.* xii. 1257.
[4] Chiozza, *Ann. Chem. Pharm.* lxxxvi. 264 ; Kraut, *loc. cit.*
[5] Stenhouse, *ibid.* lv. 1.
[6] Erdmann and Marchand, *ibid.* xliv. 344.
[7] *Arch. Pharm.* xx. 159.
[8] *Jahresb. Chem.* 1861, 418.
[9] Anschütz and Kinnicutt, *Ber. Deutsch. Chem. Ges.* xi. 1220.

Benzyl cinnamate or *Cinnameïn*, $C_9H_7O_2(C_7H_7)$, is a constituent of Peru balsam and is formed when sodium cinnamate is heated with benzyl chloride.[1] It crystallizes in prisms, which melt at 39°.

Cinnyl cinnamate or *Styracin*, $C_9H_7O_2(C_9H_9)$, is the chief constituent of liquid styrax; it is best isolated from this by filtering hot through a cloth and triturating the filtrate with cold petroleum-spirit. One-half of the liquid is then distilled off and the solution filtered from the precipitate, which consists of the ethyl cinnamate, phenylpropyl cinnamate and a portion of the styracin. The clear liquid deposits the styracin on standing in dazzling white, fascicular crystals, which melt at 44° (v. Miller).

When it is treated in ethereal solution with bromine, *phenyldibromopropyl cinnamate*, $C_9H_7O_2(C_9H_9Br_2)$, is the first product. It crystallizes in small plates and is converted by zinc and hydrochloric acid into *phenylpropyl cinnamate*, $C_9H_7O_2(C_3H_6.C_6H_5)$, which is thus obtained pure. It is a liquid, which decomposes on distillation.

The tetrabromide, $C_9H_7Br_2O_2(C_9H_9Br_2)$, is formed by the further action of bromine on styracin as a white, resinous mass, which is reduced to phenylpropyl hydrocinnamate when its ethereal solution is agitated with sodium amalgam and water.[2]

Cinnamyl oxide or *Cinnamic anhydride*, $(C_6H_5.C_2H_2.CO)_2O$, was prepared by Gerhardt by the action of cinnamyl chloride on anhydrous potassium oxalate. It is almost insoluble in cold alcohol and separates from hot alcohol as a crystalline powder, which melts at 127°.

Mixed anhydrides, which are very unstable, are formed when sodium cinnamate is treated with acetyl chloride or benzoyl chloride.[3]

Cinnamyl chloride, $C_6H_5.C_2H_2.COCl$, is formed by the action of phosphorus pentachloride on cinnamic acid; it distils at 170°—171° under a pressure of 58 mm. almost without decomposition, and solidifies on cooling to a yellowish, crystalline mass, which melts at 35—36°.[4]

Cinnamamide, $C_6H_5.C_2H_2.CO.NH_2$, is obtained by treating the chloride with ammonia; it crystallizes from hot water in plates, which melt at 141·5°.[5]

[1] Grimaux, *Zeitschr. Chem.* 1869, 157.
[2] v. Miller, *Ann. Chem. Parm.* clxxxix. 343. [3] *Ibid.* lxxxvii. 76.
[4] Rostoski, *ibid.* clxxviii. 214; Claisen and Antweiler, *Ber. Deutsch. Chem. Ges.* xiii. 2124.
[5] Rossum, *Jahresb. Chem.* 1866, 362.

Cinnamonitril, $C_6H_5.C_2H_2.CN$, is formed when the amide is heated with phosphorus chloride [1] and when cinnamic acid is distilled with lead thiocyanate.[2] It is a liquid, which boils at 254°—255° and solidifies to a mass, which melts at 11°.

Phenylallenylamidoxime, $C_6H_5.CH{=}CH.C(NOH)NH_2$, is the product of the combination of the nitril with hydroxylamine and crystallizes from dilute alcohol in pointed prisms, melting at 93°.[3]

Distyrenic acid, $C_{17}H_{16}O_2$, is prepared by heating 1 part of cinnamic acid with 4 parts of sulphuric acid and 4 parts of water for some time:

$$2C_9H_8O_2 = C_{17}H_{16}O_2 + CO_2.$$

Distyrolene is also formed in this reaction.

Distyrenic acid is an amorphous mass, which is slightly soluble in water, readily in alcohol, softens when heated and becomes completely liquid at 50°. It can be distilled almost without decomposition, forms amorphous salts and is oxidized to benzoic acid by chromic acid solution.[4]

HALOGEN DERIVATIVES OF CINNAMIC ACID.

2394 The hydrogen both of the nucleus and the side-chain of cinnamic acid may be replaced by halogens. The compounds of the latter class will be described under phenylhydroxyacrylic acid. Those which contain halogens in the nucleus have been prepared from amidocinnamic acid by means of the diazo-reaction; they crystallize for the most part badly, in contradistinction to the corresponding derivatives of hydrocinnamic acid.[5]

Chlorocinnamic Acids, $C_6H_4Cl.C_2H_2.CO_2H$.

	Melting-point.
Ortho, indistinct, yellow crystals	200°
Meta, indistinct, yellowish needles . . .	167°
Para, yellowish, crystalline mass	240°—242°

[1] Rossum, *Zeitschr. Chem.* 1866, 362.
[2] Krüss, *Ber. Deutsch. Chem. Ges.* xvii. 1768.
[3] Wolff, *ibid.* xix. 1507.
[4] Erdmann and Fittig, *Ann. Chem. Pharm.* ccxvi. 179.
[5] Gabriel, *Ber. Deutsch. Chem. Ges.* xv. 2291; Gabriel and Herzberg, *ibid.* xvi. 2036.

BROMOCINNAMIC ACIDS, $C_6H_4Br.C_2H_2.CO_2H$.

	Melting-point.
Ortho, fine, flat needles	211°—213°
Meta, long, faintly yellow needles . . .	178°—179°
Para, yellow or brownish needles . . .	251°—253°

IODOCINNAMIC ACIDS, $C_6H_4I.C_2H_2.CO_2H$.

Ortho, crystals	212°—214°
Meta, melts with decomposition at . .	181°—182°
Para, indistinct crystals; decomposes without fusion.	

These compounds are converted into the corresponding derivatives of hydrocinnamic acid by heating with hydriodic acid and amorphous phosphorus.

Fluocinnamic acid, $C_6H_4F.C_2H_2.CO_2H$, is obtained in a similar manner to fluorbenzoic acid and crystallizes in white, lustrous needles, which are readily soluble in water and volatilize without decomposition on heating.[1]

NITROCINNAMIC ACIDS, $C_6H_4(NO_2)C_2H_2.CO_2H$.

2395 Beilstein and Kuhlberg found that the cinnamonitric acid or nitrocinnamic acid, which had been prepared by Mitscherlich by the nitration of cinnamic acid,[2] and which is also formed by the action of nitric acid on cinnyl alcohol,[3] is the para-compound and that the ortho-derivative is simultaneously formed.[4] In order to prepare it, 1 part of cinnamic acid is dissolved in 5 parts of nitric of sp. gr. 1·48, the solution poured into snow and the precipitate repeatedly extracted with boiling alcohol, which dissolves the ortho-acid and a portion of the para-compound. Their ethyl ethers are then prepared by passing a current of hydrochloric acid through the solution, and are

[1] Griess, *Ber. Deutsch. Chem. Ges.* xviii. 960.
[2] *Journ. Prakt. Chem.* [1] xxii. 192 ; Kopp, *ibid.* xli. 425.
[3] Wolff, *Ann. Chem. Pharm.* lxxv. 303.
[4] *Ibid.* clxiii. 126.

separated by means of cold alcohol, in which that of the ortho-acid is readily soluble while the para-ether is almost insoluble.[1] The separation may be more rapidly effected by converting the crude product directly into the ethers, separating these by alcohol and hydrolyzing with sodium carbonate solution.[2]

Orthonitrocinnamic acid is also formed when orthonitrobenzaldehyde is boiled with acetic anhydride and sodium acetate [3] and when orthonitrobenzidene chloride is heated with sodium acetate.[4] It crystallizes in needles, which melt at 240°, are insoluble in water and only dissolve slightly in cold alcohol. Its solution in concentrated sulphuric acid becomes coloured blue on standing or when gently warmed.[5] Chromic acid solution oxidizes it to orthonitrobenzoic acid.

If it be brought into bromine or submitted to the action of bromine vapour, combination takes place, but does not occur when the operation is carried on in the sunlight. The *orthonitrophenyldibromopropionic acid*, $C_6H_4(NO_2)CHBr.CHBr.CO_2H$, which is thus obtained, crystallizes from benzene in short needles, which melt with decomposition at about 180°, a trace of indigo being formed. It forms a colourless solution in alkalis, which becomes yellow after some time or on heating, orthonitrophenylpropiolic acid and then isatin being formed. When the aqueous solution is heated with caustic soda solution, a small amount of crystallized indigo blue is obtained, while indol is formed when the acid is heated with zinc dust and caustic soda (Baeyer).

Ethylorthonitrocinnamate, $C_6H_4(NO_2)C_2H_2.CO_2.C_2H_5$, forms thin needles or rhombic crystals, melting at 44° (Baeyer).

Metanitrocinnamic acid is obtained by boiling metanitrobenzaldehyde with acetic anhydride and sodium acetate. It crystallizes from alcohol in fine needles and is precipitated from an ammoniacal solution by sulphuric acid as a snow-white crystalline powder, melting at 196°—197°.[6] It yields metanitrobenzoic acid on oxidation.

Ethyl metanitrocinnamate crystallizes from alcohol in long, pointed needles, melting at 78°—79°.

[1] Morgan, *Jahresb. Chem.* 1877, 788.
[2] Müller, *Ann. Chem. Pharm.* ccxii. 124.
[3] Gabriel and Meyer, *Ber. Deutsch. Chem. Ges.* xiv. 830.
[4] Bad. Anilin- und Sodafabrik, *ibid.* xv. 969.
[5] Baeyer, *Ber. Deutsch. Chem. Ges.* xiii. 2257.
[6] R. Schiff, *ibid.* xi. 1782; Tiemann and Oppermann, *ibid.* xiii. 2060; Friedländer and Lazarus, *Ann. Chem. Pharm.* ccxxix. 233.

Paranitrocinnamic acid is only slightly soluble in boiling alcohol, from which it crystallizes in prisms, melting at 288°.[1] Chromic acid oxidizes it to paranitrobenzoic acid.

Ethyl paranitrocinnamate forms very fine needles, which melt at 138·5° and are almost insoluble in cold alcohol and ether.

AMIDOCINNAMIC ACIDS, $C_6H_4\begin{cases}NH_2\\CH=CH.CO_2H\end{cases}$.

2396 *Orthamidocinnamic acid* cannot be prepared by the reduction of orthonitrocinnamic acid with ammonium sulphide or tin and hydrochloric acid, since its inner anhydride, carbostyril, is always formed. It is readily obtained however by treating the solution of the nitro-acid in caustic baryta with ferrous sulphate.[2]

In order to prepare it, 150 grms. of orthonitrocinnamic acid and 2,100 grms. of crystallized barium hydroxide are dissolved in 30 litres of hot water, 1,400 grms. of ferrous sulphate are added and the whole heated to 95°—100° for two hours. Carbon dioxide is then passed through the liquid and the filtrate concentrated; barium amidocinnamate crystallizes out and a second crop is obtained by evaporation of the mother-liquor. The total quantity is dissolved in 750 cb. cm. of hot 4 per cent. hydrochloric acid, the barium precipitated with sodium sulphate, the solution boiled up with animal charcoal, filtered and neutralized with caustic soda and finally treated with sodium acetate, which precipitates the larger portion of the amido-acid, the remainder crystallizing out on cooling.[3]

Orthamidocinnamic acid forms a yellow, crystalline powder, or needles, which melt at 158°—159° with evolution of gas. It is tolerably soluble in hot water and alcohol, forming solutions which have a strong bluish green fluorescence.

When it is dissolved in hot, dilute hydrochloric acid, the hydrochloride, $C_9H_9NO_2.ClH$, crystallizes on cooling in warty masses of hard, compact prisms.

[1] Drewsen, *Ann. Chem. Pharm.* cclxii. 150.
[2] Tiemann and Oppermann, *Ber. Deutsch. Chem. Ges.* xiii. 2061.
[3] Fischer and Kuzel, *Ann. Chem. Pharm.* ccxxi. 266.

Ethyl orthamidocinnamate, $C_6H_4(NH_2)C_2H_2.CO.OC_2H_5$, is readily prepared by the reduction of the corresponding nitrocinnamic ether with tin and hydrochloric acid and is precipitated by sodium acetate, after the removal of the tin by sulphuretted hydrogen, in light yellow needles, which melt at 77°—78° and readily dissolve in alcohol, forming a yellow solution, which has a strong yellowish-green fluorescence. Its hydrochloride forms colourless needles and is partially dissociated when its solution is heated, the liquid being yellow while hot and becoming colourless again on cooling.

Since the ether is quantitatively hydrolyzed by alcoholic potash, orthamidocinnamic acid can also be readily prepared from the ether of orthonitrocinnamic acid.[1]

Ethyl orthamidocinnamic acid, $C_6H_4(NH.C_2H_5)C_2H_2.CO_2H$ is formed when orthamidocinnamic acid and ethyl iodide are heated with alcoholic potash. It is only slightly soluble in water, readily in alcohol, forming a yellowish solution with a green fluorescence, and separates from high-boiling petroleum-ether in fascicular groups of yellow needles, which melt at 125°.[2]

Dicthylorthamidocinnamic acid, $C_6H_4N(C_2H_5)_2C_2H_2.CO_2H$, is formed along with the preceding compound and crystallizes from alcohol in light, citron-yellow plates, which melt at 124° and form a yellow solution in alcohol, which has a bluish-green fluorescence.

Nitroso-ortho-ethylamidocinnamic acid, $C_6H_4N(C_4H_5)(NO)C_2H_2.CO_2H$, is formed by the action of sodium nitrite on a cooled solution of ethylamidocinnamic acid in dilute sulphuric acid and crystallizes from dilute alcohol in yellowish, lustrous plates, which melt with decomposition at 150°.

α-Nitro-orthamidocinnamic acid, $C_6H_3(NO_2)(NH_2)C_2H_2.CO_2H$. Two isomeric acids are formed when 1 part of orthamidocinnamic acid is dissolved in 5 parts of sulphuric acid and a solution of 3 parts of saltpetre in 10 parts of sulphuric acid added, the temperature not being allowed to rise above 0°. If the solution be poured upon ice and diluted with a large amount of water, the *β*-compound separates out after some time. The *α*-compound, which is the chief product, crystallizes from the mother-liquor after the addition of caustic soda solution until the reaction is only faintly acid. It forms light

[1] Friedländer and Weinberg, *Ber. Deutsch. Chem. Ges.* xv. 1422.
[2] *Ibid.*; Fischer and Kuzel, *Ann. Chem. Pharm.* ccxxi. 267.

brownish-red needles, which melt at 240°, are only slightly soluble in water and dissolve readily in alcohol.

β-Nitro-orthamidocinnamic acid crystallizes in brownish-yellow needles, which melt at 254° and are almost insoluble in water.[1]

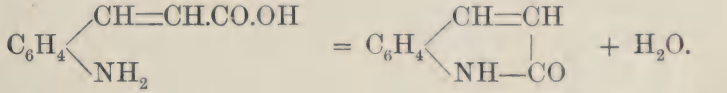
Metamidocinnamic acid is obtained in a similar manner to the ortho-acid. It crystallizes from hot water in long stellate or fan-shaped groups of light greenish-yellow needles, melting at 180°—181°. It combines both with acids and bases.

Paramidocinnamic acid crystallizes from hot water in fine, light yellow needles, grouped in spherical aggregates, which melt at 175°—176°. The reactions of this substance and its isomerides have been investigated by Tiemann and Oppermann.[2]

[1] Friedländer and Lazarus, *Ann. Chem. Pharm.* ccxxix. 241.
[2] *Ber. Deutsch. Chem. Ges.* xiii. 2067.

THE CARBOSTYRIL GROUP.

2397 *Carbostyril*, C_9H_7NO, was prepared by Chiozza by heating crude nitrocinnamic acid with ammonium sulphide,[1] while Kühner obtained it from the same source by reduction with tin and hydrochloric acid.[2] Morgan, who prepared it in the same way from pure nitrocinnamic acid, found that it is also formed when the ethyl ether of this acid is heated gently with ammonium sulphide.[3] It is therefore formed from orthamidocinnamic acid by the elimination of water:



The free amido-acid cannot however be directly converted into carbostyril, but shows a great tendency to form a resinous mass, and decomposes on heating. Carbostyril is however formed when acetylorthamidocinnamic acid is heated.[4] It is also formed, according to the researches of Tiemann and Oppermann, as a by-product in the preparation of orthamidocinnamic acid, and is readily obtained by heating an acid aqueous solution of the hydrochloride for some time.[5] In order to prepare carbostyril, ethyl orthonitrocinnamate is heated on the water-bath with alcoholic ammonium sulphide. The compound of ammonia with hydroxycarbostyril (see below) separates on cooling in flakes, which are filtered off. The filtrate is then evaporated and the residue extracted with a very dilute, hot solution of sodium carbonate. The carbostyril is then precipitated by passing carbon dioxide through the liquid, while hydroxycarbostyril

[1] *Ann. Chem. Pharm.* lxxxiii. 117. [2] *Zeitschr. Chem.* 1865, 2.
[3] *Chem. News*, xxxvi. 269.
[4] Baeyer and Jackson, *Ber. Deutsch. Chem. Ges.* xiii. 115.
[5] *Ibid.* xiii. 2069.

remains in solution and is finally separated by the addition of sulphuric acid.[1]

Carbostyril may be even more readily prepared by heating ethyl orthamidocinnamate with hydrochloric acid in a sealed tube.[2] It is scarcely soluble in cold, readily in hot water and alcohol, and crystallizes in large, lustrous prisms, which melt at 199°—200° and sublime in needles at a higher temperature. Potassium permanganate oxidizes it in alkaline solution to isatin and oxalortho-amidobenzoic acid,[3] which is formed according to the following equation:

$$C_6H_4\left\langle\begin{array}{l}CH{=}CH\\ \quad\quad\;\;|\\ NH{-}CO\end{array}\right. + 4O = C_6H_4\left\langle\begin{array}{l}CO.OH\\ \\ NH{-}CO.CO.OH.\end{array}\right.$$

Pseudo-isatin is then formed by loss of water and carbon dioxide and immediately passes into isatin.

Carbostyril contains one atom of hydrogen which can be replaced by metals and alcohol radicals. Phosphorus pentachloride converts it into monochloroquinoline, C_9H_6ClN (p. 168), which is reconverted into carbostyril by water at 120°.

Methylcarbostyril, $C_9H_6NO(CH_3)$, is obtained by heating chloroquinoline with sodium methylate and methyl alcohol. It is an oily liquid, which smells like oranges and boils at 246°—247°.

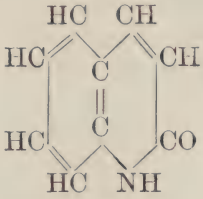
Ethylcarbostyril, $C_9H_6NO(C_2H_5)$, is formed when carbostyril is heated with ethyl iodide and alcoholic potash, as well as when chloroquinoline is heated with alcoholic potash, and may also be obtained by heating ethyl orthamidocinnamate with a concentrated alcoholic solution of zinc chloride.[4] It is an oily liquid, which has a sweetish, penetrating odour, boils with slight decomposition at 250° and solidifies in a freezing mixture to crystals, which melt below 0°. It combines with acids to form deliquescent salts; it is very stable towards alkalis, but is reconverted into carbostyril by dilute hydrochloric acid at 120°.

Phenylcarbostyril, $C_9H_6NO(C_6H_5)$, is obtained by heating a solution of chloroquinoline with sodium phenate and phenol; it crystallizes from alcohol in lustrous plates, melting at 68°—69°.

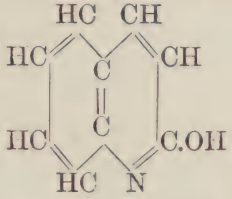
[1] Friedländer and Ostermaier, *Ber. Deutsch. Chem. Ges.* xiv. 1916.
[2] Friedländer and Weinberg, *ibid.* xv. 1421.
[3] Friedländer and Ostermaier, *ibid.* xv. 332.
[4] Friedländer and Weinberg, *ibid.* xv. 2013.

In view of the formation and decompositions of chloroquinoline, carbostyril must be considered as hydroxyquinoline and its constitution expressed by the following tautomeric formulæ:

Carbostyril.



Hydroxyquinoline.



According to the first formula it is the lactam, according to the second the lactim, of orthamidocinnamic acid.

α-Nitrocarbostyril, $C_9H_6(NO_2)NO$, is formed when *α*-nitro-orthamidocinnamic acid is heated to 150° with hydrochloric acid, and crystallizes from alcohol in fine needles, which remain solid at 320°.

β-Nitrocarbostyril is obtained in a similar manner from the *β*-acid and is also formed, together with the ethyl ether of the *α*-acid, by the nitration of ethyl orthamidocinnamate. It is almost insoluble in alcohol, and crystallizes from hot, glacial acetic acid in thick, yellow needles, melting at 260°, forms a brick-red solution in caustic soda and is reprecipitated by carbon dioxide.

γ-Nitrocarbostyril is prepared by the action of a mixture of nitric and sulphuric acids on carbostyril. It crystallizes from acetic acid in long, white needles, which melt at 200° and form a yellow solution in caustic soda.

γ-Amidocarbostyril, $C_9H_6(NH_2)NO$, is formed by the reduction of the preceding compound with tin and hydrochloric acid. It crystallizes from glacial acetic acid in slightly soluble, yellow plates, which do not melt below 320°.[1]

2398 *Cynurin*, C_9H_7NO. Liebig, in 1853, discovered a new acid in the urine of the dog and named it *cynurenic acid*, in order to indicate its source. On heating, it yielded a sublimate, which differed from the original acid, and on dry distillation it gave an oily liquid, smelling like benzonitril. Two analyses gave numbers which led to the composition $C_{16}H_{14}N_2O_5$,[2] while Schmiedeberg and Schulten found that its formula is $C_{20}H_{14}N_2O_6$, and that it decomposes on heating into carbon dioxide and

[1] Friedländer and Lazarus, *Ann. Chem. Pharm.* ccxxix. 245.
[2] *Ibid.* lxxxvi. 125; cviii. 354; cxl. 143.

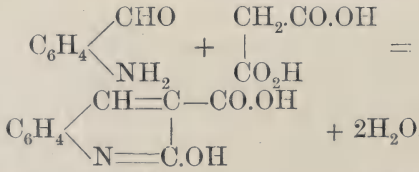
cynurin,[1] $C_{18}H_{14}N_2O_2$. This substance was recognized by Kretschy as a hydroxyquinoline and the cynurenic acid as hydroxyquinolinecarboxylic acid, $C_9H_6NO(CO_2H)$. According to him, it is formed in considerable quantity when a diet consisting exclusively of flesh is administered.[2]

In order to extract it from dog's urine, a considerable amount of this is treated with dilute hydrochloric acid (1 in 10) and precipitated with phosphotungstic acid, the precipitate being then decomposed by baryta.[3] It is scarcely soluble in cold water; when it is set free from a hot solution in ammonia by the addition of acetic acid and the whole allowed to cool, it crystallizes in brilliant needles, containing one molecule of water, which is lost at 140°—145°. On evaporation with hydrochloric acid and potassium chlorate, a reddish residue is left, which becomes brownish green and then emerald green when moistened with ammonia; the intensity of the colouration increases on exposure to the air.[4]

Cynurenic acid melts at 253°—258° and decomposes into carbon dioxide and cynurin, which crystallizes from hot water on rapid cooling in needles containing three molecules of water, but on gradual cooling in anhydrous, lustrous, monosymmetric prisms or tablets, which have a bitter taste and a faint alkaline reaction. Its hydrochloride crystallizes in needles, which readily lose hydrochloric acid.

Cynurin melts at 201°, sublimes very slowly when further heated and boils with decomposition at 300°, an oily liquid being formed. Phosphorus pentachloride converts it into monochloroquinoline, which crystallizes well but is very unstable. When cynurin or cynurenic acid is heated with zinc dust in a current of hydrogen, it is reduced to quinoline, while potassium permanganate oxidizes them to oxalorthamidobenzoic acid.[5]

Cynurin is therefore very similar to the isomeric carbostyril; when orthamidobenzaldehyde is heated to 120° with malonic acid, carbostyrilcarboxylic acid, isomeric with cynurenic acid, is formed:



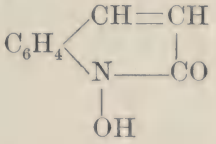
[1] *Ann. Chem. Pharm.* clxiv. 155.
[2] *Monatsh. Chem.* ii. 57.
[3] Hofmeister, *Ber. Deutsch. Chem. Ges.* xiv. 688.
[4] Jaffé, *ibid.* xvi. 1511.
[5] Kretschy, *Monatsh. Chem.* v. 16.

This is very slightly soluble in water, but more readily in boiling alcohol, from which it crystallizes in broad needles or long-pointed prisms, which melt above 320°.[1]

2399 *α-Hydroxycarbostyril*, $C_9H_7NO_2$, is formed, as stated above, in the preparation of carbostyril, which it resembles very closely. It melts at 190·5° and sublimes in fine needles at a higher temperature. It crystallizes from hot water, in which it is only slightly soluble, in nacreous plates, which like those of orthnitrocinnamic acid become deep red on exposure to light. It is a strong monobasic acid and decomposes carbonates; when its solution is heated with a few drops of nitric acid, it becomes coloured deep red. It is reduced by zinc dust and hydrochloric acid to carbostyril and is oxidized by potassium permanganate to orthonitrobenzoic acid.

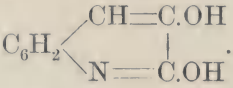
Ethoxycarbostyril, $C_6H_6NO_2(C_2H_5)$, is obtained by heating the potassium salt of oxycarbostyril with ethyl iodide. It crystallizes from a mixture of ether and petroleum-ether in splendid thick prisms, which melt at 73° and volatilize at a higher temperature without decomposition. It is a strong base (Friedländer and Ostermaier).

α-Hydroxycarbostyril is probably an isonitroso-compound :



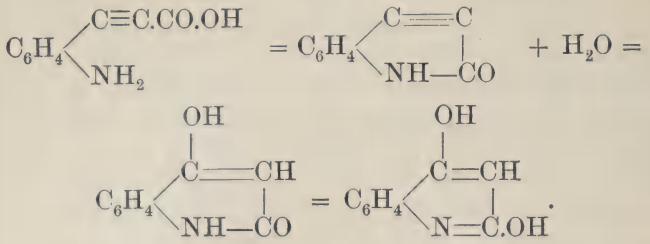
Its oxidation to orthonitrobenzoic acid is readily explained by this formula.

β-Hydroxycarbostyril or *α-β-Dihydroxyquinoline.* When the *α-β*-dichloroquinoline, which is obtained from hydrocarbostyril (p. 168) is heated to 120° with dilute hydrochloric acid, *β-chlorocarbostyril*, C_9H_6ClN, is formed; it resembles carbostyril and melts at 241°—242°. On fusion with potash it is converted into β-hydroxycarbostyril, which is a feeble base and is precipitated by water from its solution in hydrochloric acid in needles, which melt above 300° and sublime. It is simultaneously a weak monobasic acid of the following constitution :[2]



[1] Friedländer and Göhring, *Ber. Deutsch. Chem. Ges.* xvii. 459.
[2] Friedländer and Weinberg, *ibid.* xv. 2679.

γ-Hydroxycarbostyril or *α-γ-Dihydroxyquinoline* is formed when orthamidophenylpropiolic acid is heated with sulphuricacid:

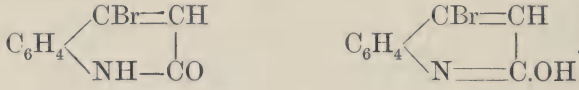


It behaves in a very similar manner to the *β*-compound and crystallizes in needles, which sublime above 320° without melting.[1]

γ-Chlorocarbostyril, C_9H_6ClNO, is formed when the amido-acid is boiled with hydrochloric acid, and crystallizes from hot alcohol in silky needles, melting at 246°, which sublime at a higher temperature. On heating with phosphorus pentachloride, *α-γ-dichloroquinoline*, which melts at 67°, is formed.

γ-Bromocarbostyril, C_9H_6BrNO, is obtained by boiling amido-propiolic acid with hydrobromic acid and by treating ethylcarbostyril with bromine vapour, an unstable addition-product being first formed, which readily decomposes with formation of ethyl-bromocarbostyril. The latter is then converted into γ-bromocarbostyril by heating to 120° with hydrochloric acid (Friedländer and Weinberg).

Its constitution is expressed by the following tautomeric formulæ:



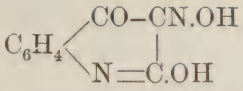
It crystallizes from alcohol in needles, which melt at 266°. The following remarkable relation exists between the three closely connected acids, orthamidohydrocinnamic acid, orthamidocinnamic acid, and orthamidopropiolic acid. The first changes immediately into its inner anhydride, the second can only be converted into an anhydride under certain conditions, while the anhydride of the third has not yet been obtained, since when the side-chains join to form a ring, this is invariably accompanied by the addition of water, hydrochloric acid, &c., to the triple-linked carbon atom (Baeyer).

[1] Baeyer and Bloem, *Ber. Deutsch. Chem. Ges.* xv. 2147.

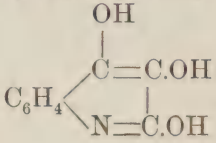
2400 *Quinisatic acid*, $C_9H_7NO_4$. When a solution of γ-hydroxycarbostyril and sodium nitrite is poured into dilute sulphuric acid, a brick-red precipitate of *nitroso-γ-hydroxycarbostyril*, $C_9H_6N_2O_3$, is formed, which crystallizes from alcohol in small orange-yellow prisms and is converted into *β-γ-dihydroxycarbostyril* by treatment with stannous chloride and subsequent oxidation in the air. This substance, which crystallizes in long needles, is oxidized to quinisatic acid by ferric chloride.

The constitution of these compounds is probably expressed by the following formulæ:

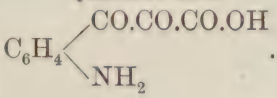
Nitroso-γ-hydroxycarbostyril.



β-γ-Dihydroxycarbostyril.



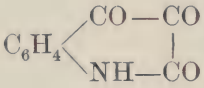
Quinisatic Acid.

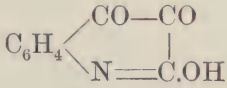


Quinisatic acid is tolerably soluble in cold, very readily in hot water, from which it crystallizes in straw-yellow prisms. Its alkali salts are almost colourless and readily soluble; the silver salt is a yellowish-green, very unstable precipitate.

Quinisatin, $C_9H_5NO_3$, is formed when quinisatic acid is heated to 120°—125°, the crystals becoming red without undergoing any alteration in form. It forms a yellowish-red solution in absolute alcohol and is reconverted into quinisatic acid when covered with water or allowed to lie in the air.

The constitution of quinisatin is expressed by one of the following formulæ:[1]





[1] Baeyer and Homolka, *Ber. Deutsch. Chem. Ges.* xvi. 216.

HYDRAZINE DERIVATIVES OF CINNAMIC ACID.[1]

2401 *Orthohydrazinecinnamic acid*, $C_6H_4(N_2H_3)C_2H_2.CO_2H$. In order to prepare this substance, 10 parts of orthamidocinnamic acid are dissolved in 9 parts of concentrated hydrochloric acid and 70 parts of hot water, the solution allowed to cool until crystals begin to separate out and the calculated quantity of sodium nitrite added, the liquid being well stirred and kept cool. The hydrochloride of diazocinnamic acid separates out after a short time as a yellow, crystalline powder, which is converted by a solution of normal sodium sulphite into the sodium salt of diazosulphocinnamic acid. This is reduced by the action of zinc dust and hydrochloric acid to the hydrazine compound, which is converted by hydrochloric acid into the hydrochloride of orthohydrazinecinnamic acid:

$$C_6H_4\begin{cases}CH{=}CH.CO_2H\\NH{-}NH.SO_3Na\end{cases} + H_2O + HCl =$$

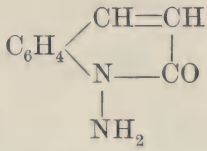
$$C_6H_4\begin{cases}CH{=}CH.CO_2H\\NH{-}NH_3Cl\end{cases} + SO_4HNa.$$

If it be dissolved in water and sodium acetate added, the free hydrazine-acid is precipitated in yellowish crystals, which are only very slightly soluble in hot water and decompose on re-crystallization or on the evaporation of their solution. Its solution in acetic acid bleaches litmus and indigo. It reduces Fehling's solution and ammoniacal silver solution, and melts at 171° with formation of acetic acid and indazol (p. 64).

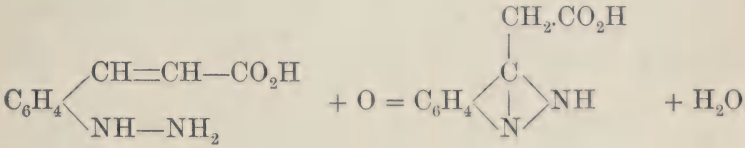
Orthohydrazinecinnamic anhydride, $C_9H_8N_2O$. This compound, which is also called *amidocarbostyril*, is formed by boiling sodium hydrazinesulphocinnamate with dilute hydrochloric acid, and crystallizes from hot water in fine needles, which melt at 127°, sublime without decomposition and do not reduce Fehling's

[1] Fischer and Kuzel, *Ann. Chem. Pharm.* ccxxi. 261; Fischer and Tafel, *ibid.* ccxxvii. 303.

solution or silver solution. It is a feeble base, the hydrochloride of which crystallizes in prisms. When sodium nitrite is added to a faintly acid solution, carbostyril is precipitated, so that it must have the following constitution :



2402 *Indazolacetic acid*, $C_9H_8N_2O_2$, is very readily obtained by agitating an alkaline solution of hydrazinecinnamic acid in the air until it no longer reduces Fehling's solution :



The indazolacetic acid separates out on the addition of hydrochloric acid and crystallizes from hot water in fine needles, which are generally slightly yellow and decompose at 168°—170° into carbon dioxide and methylindazol.

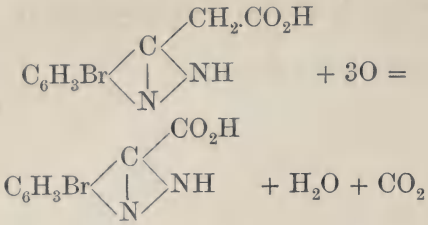
The copper salt, $(C_9H_7N_2O_2)Cu + 2H_2O$, is a characteristic compound. It separates on the addition of copper acetate to a solution of the acid in dilute acetic acid as a pale green, viscid precipitate, which is quite insoluble in hot water, but crystallizes from hot alcohol in fine needles, which, after drying in a vacuum, form an extremely light powder.

Indazolacetic acid also combines with acids.

Monobromindazolacetic acid, $C_6H_3Br(CN_2H)CH_2.CO_2H$. In order to prepare this compound, indazolacetic acid is dissolved in dilute hydrochloric acid and an equal weight of bromine dissolved in water added. The precipitate is treated with animal charcoal and recrystallized first from glacial acetic acid and then from water. It is thus obtained in matted needles, which melt at 200° with a vigorous evolution of gas.

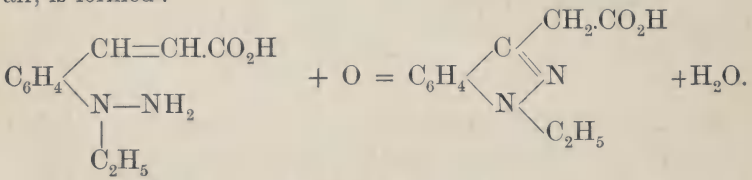
Monobromindazolcarboxylic acid, $C_8H_5BrN_2O_2$. Indazolacetic acid itself is completely destroyed by the usual oxidizing agents, while the monobromo-derivative is converted by a

solution of chromic acid in acetic acid into bromindazolcarboxylic acid:



This is almost insoluble in water and dilute hydrochloric acid, and crystallizes from hot glacial acetic acid in matted needles, which are readily soluble in the alkalis and their carbonates. On heating with water to 200°, it decomposes into carbon dioxide and bromindazol.

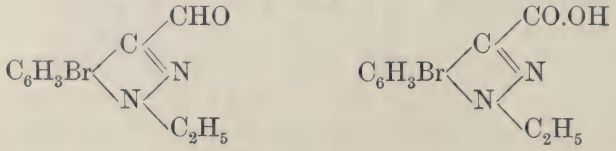
Ethylisindazolacetic acid, $C_{11}H_{12}N_2O_2$. When nitro-ortho-ethylamidocinnamic acid is reduced with zinc and acetic acid, the corresponding hydrazine acid, which rapidly oxidizes in the air, is formed:



The ethylisindazolacetic acid thus obtained separates from hot water as an oil, which rapidly solidifies to fine plates, melting at 131°. If these be dissolved in chloroform and the solution diluted with petroleum-spirit, aggregates of fine plates, melting at 126°, are obtained, which change into compact crystals, melting at 131°, when left in contact with the mother-liquor; it decomposes at 162° into carbon dioxide and ethylmethisindazol.

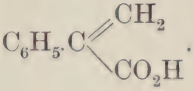
Ethylbromisindazolacetic acid, $C_{11}H_{11}BrN_2O_2$, is formed by the action of bromine on an acetic acid solution of the preceding compound. It crystallizes from hot water in fan-shaped aggregates of needles.

Ethylbromisindazolcarboxylic acid, $C_{10}H_9BrN_2O_2$, is obtained by the oxidation of the preceding compound, the aldehyde being formed as an intermediate product:



The latter crystallizes from wood-spirit in long prisms, which melt at 88° and volatilize without decomposition. The acid forms characteristic, bent needles, which melt at about 210° and decompose when more strongly heated into carbon dioxide and ethylbromisindazol.

ATROPIC ACID, OR α-PHENYLACRYLIC ACID,



2403 This compound was first prepared by Kraut, who treated atropine with baryta water [1] and was then obtained by Lossen by heating the same substance with hydrochloric acid,[2] the tropic acid, $C_6H_5.CH(CH_2.OH)CO_2H$, which is the first product, decomposing into water and atropic acid. It is also formed when ethylatrolactic acid, $C_6H_5.C(CH_3)(OC_2H_5)CO_2H$, is boiled with hydrochloric acid [3] and when chlorohydratropic acid is heated with caustic soda.[4]

In order to prepare it, 1 part of atropine is boiled with 2 parts of barium hydroxide and 20 parts of water for 15 hours, evaporated to some extent and filtered. Hydrochloric acid is then added to the hot filtrate and the whole allowed to cool. The greater portion of the atropic acid separates on cooling, the remainder being extracted with ether.[5] It crystallizes from hot water in needles and from alcohol in monosymmetric tablets, which melt at 106°—107°, are volatile with steam and boil with decomposition at about 267°. It is oxidized by chromic acid to benzoic acid, while formic and phenylacetic acids are formed when it is fused with caustic potash.

It is reduced by nascent hydrogen to hydratropic acid.

It differs from the isomeric cinnamic acid in that it dissolves in 692 parts of water at 19° and is not precipitated from a neutral solution by manganese chloride.

[1] *Ann. Chem. Pharm.* cxxviii. 282.
[2] *Ibid.* cxxxviii. 230.
[3] Ladenburg and Rügheimer, *Ber. Deutsch. Chem. Ges.* xiii. 2042.
[4] Spiegel, *ibid.* xiv. 237.
[5] Fittig and Wurster, *Ann. Chem. Pharm.* cxcv. 147.

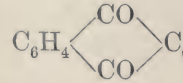
Calcium atropate, $(C_9H_7O_2)Ca + 5H_2O$, forms large, monosymmetric crystals, which dissolve in 43 parts of water at 18° (Kraut.)

Isatropic acid, $C_{18}H_{16}O_4$. Lossen discovered that isatropic acid is formed in addition to atropaïc and tropaïc acids when atropine is heated with hydrochloric acid.[1] Fittig and Wurster then observed that this substance is always formed in small quantity when atropic acid is recrystallized from boiling water, more largely when the solution is boiled for some time or the acid heated alone,[2] and Fittig has finally shown that two isomeric acids are thus formed.[3]

α-Isatropic acid is the chief product and is almost exclusively formed when atropic acid is gradually heated to 140°—160° for 24—36 hours in a closed flask. After cooling, it is heated with a little acetic acid or alcohol, again allowed to cool, the coloured liquid poured off and the residue recrystallized from acetic acid. It forms small crystals united to crusts or warty masses, melts at 237°—237·5°, is only very slightly soluble in water and is almost insoluble in ether. When slowly distilled it decomposes almost completely into atronol, $C_{16}H_{14}$, carbon monoxide and carbon dioxide, while on rapid heating atronic acid, $C_{17}H_{14}O_2$, is also formed, a portion of the *α*-acid passes over unchanged and a second portion is converted into the *β*-acid.

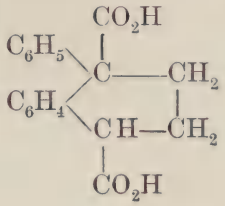
It does not combine with bromine in the cold and is not altered by the action of water and sodium amalgam.[4]

β-Isatropic acid is formed in relatively large amount when the acid is boiled with water, crystallizes from hot water in small, lustrous, quadratic tablets and separates from acetic acid either in thick, transparent, four-sided tablets, or in druses of apparently octahedral crystals, which contain a molecule of acetic acid. It melts at 206° and is converted at 220°—225° into the *α*-acid.

These acids have identical chemical properties. On oxidation with chromic acid they yield carbon dioxide, acetic acid, orthobenzoylbenzoic acid, $C_6H_5.CO.C_6H_4.CO_2H$, and anthraquinone,  These compounds and the other decomposition products of the acids in question will be subsequently described.

[1] *Ann. Chem. Pharm.* cxxxviii. 237.
[2] *Ibid.* cxcv. 147.
[3] *Ibid.* ccvi. 34.
[4] Kraut, *ibid.* cxlviii. 246.

The two isatropic acids appear to be physical isomerides and probably have the following constitution :



PHENYLHYDROXYACRYLIC ACIDS.

2404 The two isomeric acids which can exist according to theory :

$$C_6H_5.CH{=}\overset{\alpha}{C}(OH)CO_2H \qquad C_6H_5.\overset{\beta}{C}(OH){=}CH.CO_2H$$

are unknown, since they are immediately converted into the isomeric phenylglycidic acid. Their derivatives have, however, been prepared.

Phenoxycinnamic acid, $C_6H_5.CH{=}C(OC_6H_5)CO_2H$, is formed, together with cinnamic acid, when sodium phenylglycolate (Pt. III. p. 111) is heated with benzaldehyde and acetic anhydride, and crystallizes from alcohol in prisms, which melt at 179°—180°.[1]

α-Chlorocinnamic acid or *Phenyl-α-chloracrylic acid*, $C_6H_5.CH{=}CCl.CO_2H$, is obtained, accompanied by the β-acid, by the action of alcoholic potash on phenyldichloropropionic acid. It is the chief product of the reaction and can readily be separated from the isomeric acid by means of its potassium salt, which is only slightly soluble in alcohol.[2] It is also formed when benzaldehyde is heated with acetic anhydride and sodium chloracetate[3] and by the action of phosphorus pentachloride on the ethyl ether of benzoylacetic acid, $C_6H_5.CO.CH_2CO_2H$, the β-acid being probably first formed and then converted into the α-compound, exactly as in the case of the corresponding bromine compound.[4]

[1] Oglialoro, *Gaz. Chim. Ital.* x. 481.
[2] Jutz, *Ber. Deutsch. Chem. Ges.* xv. 758.
[3] Plöchl, *ibid.* xv. 1945.
[4] Perkin, *Journ. Chem. Soc.* 1885, i. 256.

α-Chlorocinnamic acid crystallizes from petroleum-spirit in long, thin needles, which melt at 142° and are slightly soluble in cold, somewhat more readily in hot water.

β-Chlorocinnamic acid or *Phenyl-β-chloracrylic acid*, $C_6H_5.CCl=CH.CO_2H$, forms long plates, melting at 114°.

α-Bromocinnamic acid or *Phenyl-α-bromacrylic acid*, $C_6H_5.CH=CBr.CO_2H$, was obtained by Glaser, together with the *β*-acid, by the action of alcoholic potash on phenyldibromopropionic acid,[1] *β*-phenylbromethylene being simultaneously formed.[2] When hydrochloric acid is added to the product, the *α*-acid is first precipitated, then a mixture of the isomerides and finally the *β*-acid, which is the chief product. *α*-Bromocinnamic acid crystallizes from hot water in long, four-sided needles, which melt at 130°—131°.[3]

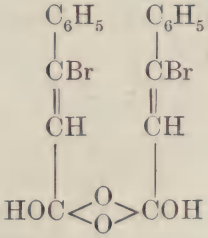
β-Bromocinnamic acid or *Phenyl-β-bromacrylic acid*, $C_6H_5.CBr=CH.CO_2H$, is very readily soluble in boiling water and separates in large, six-sided tablets, which melt at 120° and are converted into the *α*-acid by distillation or by heating with hydriodic acid; its ether also undergoes this change on distillation at the ordinary pressure and both the ethers are converted by phosphorus pentachloride into the same *bromocinnamyl chloride*, $C_6H_5.C_2HBr.COCl$, which is an oily liquid and is decomposed by water with formation of the *α*-acid.[4]

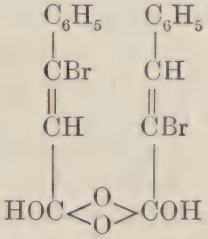
Michael and Brown have obtained a third bromocinnamic acid by the combination of hydrobromic acid with phenylpropiolic acid, $C_6H_5.C\equiv C.CO_2H$, which crystallizes in long, flat needles or rhombic tablets, melts at 158·5° and is converted into benzoylacetic acid by being dissolved in sulphuric acid.[5] Erlenmeyer, on the other hand, found that the acid which is thus formed melts at 153·5° and yields phenylpropiolic acid, together with phenylacetylene and *β*-bromostyrolene, on treatment with sodium carbonate solution. Concentrated sulphuric acid converts it into benzoylacetic acid and acetophenone, while it is decomposed into acetophenone and a little phenylacetaldehyde by the action of hot hydrobromic acid. When its solution in glacial acetic acid is saturated with hydrobromic acid, an isomeric acid, which melts at 159°—160°, is formed. It is probably identical with the compound obtained by Michael and

[1] *Ann. Chem. Pharm.* cxlvii. 330.
[2] Barisch, *Journ. Prakt. Chem.* [2] xx. 173.
[3] Glaser; Plöchl; Barisch, *loc. cit.*
[4] Anschütz and Selden, *ibid.* xx. 1382.
[5] *Ber. Deutsch. Chem. Ges.* xix. 1378.

Brown and also yields acetophenone and a large amount of phenylacetaldehyde on heating with hydrobromic acid.

According to Erlenmeyer's views, the acid of lower melting-point is a compound of two molecules of β-bromocinnamic acid, while the other contains equal molecules of the α- and β-acids.[1]





Wislicenus, on the other hand, assumes that these four bromocinnamic acids have the same molecular weight and are derived from two geometrically isomeric cinnamic acids, which stand in the same relation to one another as fumaric to maleic acid (Pt. II. p. 216).

Only one of these is known, its constitution being probably that represented by Fig. 2, the other (Fig. 3) is still to be discovered :

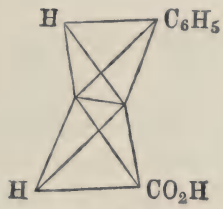


FIG. 2.

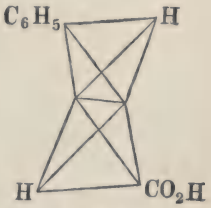


FIG. 3.

It also appears from these figures that each of these acids can yield two monobrominated derivatives.[2]

2405 *Orthonitro-β-hydroxycinnamic acid*, $C_6H_4(NO_2)C(OH)=CHCO_2H$, is obtained by the action of alcoholic potash on orthonitrophenylchlorolactic acid ; it crystallizes from hot water in flat needles, which decompose on heating, with elimination of carbon dioxide and formation of a small amount of indigo.[3]

[1] *Ber. Deutsch. Chem. Ges.* xix. 1936.
[2] *Räumliche Anordnung der Atome*, 47.
[3] Baeyer, *Ber. Deutsch. Chem. Ges.* xiii. 2262.

Paranitro-β-hydroxycinnamic acid is formed, together with paranitrochlorostyrolene and paranitrophenylchlorolactic acid, by the action of hypochlorous acid on sodium paranitrocinnamate, and forms small crystals, which decompose on heating.[1]

Paranitrophenylnitro-acrylic acid or *α-4-Dinitrocinnamic acid*, $C_6H_4(NO_2)CH=C(NO_2)CO_2H$, is deposited in snow-white, glistening plates, when a solution of paranitrocinnamic and sulphuric acids is allowed to run into a mixture of nitric and sulphuric acids at a temperature of — 20°. It loses carbon dioxide even at 0° and decomposes quantitatively into this and *ω*-4-dinitrostyrolene in aqueous solution (p. 35).

Ethyl paranitrophenylnitro-acrylate, $C_6H_4(NO_2)C_2H(NO_2)CO_2C_2H_5$, is formed when ethyl paranitrocinnamate is brought into a cooled mixture of 2 parts of concentrated nitric acid with 4 parts of sulphuric acid and the solution poured upon ice. It crystallizes from hot benzene in lustrous, white flakes, which melt at 109°—110° and are oxidized to paranitrobenzoic acid by chromic acid. When boiled for some time with water, it is decomposed into paranitrobenzaldehyde, alcohol, nitromethane and carbon dioxide :

$$C_6H_4\begin{cases}CH=C(NO_2)CO.OC_2H_5\\NO_2\end{cases} + 2H_2O =$$

$$C_6H_4\begin{cases}CHO\\NO_2\end{cases} + HO.C_2H_5 + CH_3NO_2 + CO_2.$$

A similar decomposition is caused by sulphuric acid, the nitromethane being however in this case decomposed with formation of hydroxylamine, which combines with the nitrobenzaldehyde to form paranitrobenzaldoxime.

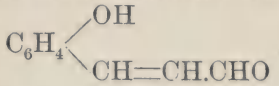
If the ether be boiled with alcohol, a reaction takes place and *ethyl paranitrophenylethoxynitropropionate*, $C_6H_4(NO_2)CH(OC_2H_5)CH(NO_2)CO_2.C_2H_5$, is formed. It crystallizes in monosymmetric prisms and melts at 52°. Similar compounds are formed by other alcohols.[2]

Metanitrophenylnitro-acrylic acid or *α-3-Dinitrocinnamic acid* is even less stable than the para-compound and decomposes at once into carbon dioxide and *α*-3-dinitrostyrolene. Its ethyl

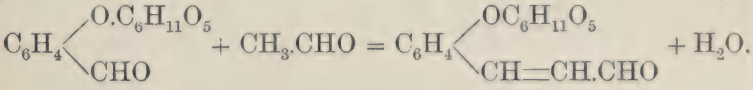
[1] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xiv. 1868.
[2] Friedländer and Mähly, *Ann. Chem. Pharm.* ccxxix. 210.

ether is obtained by the action of a mixture of nitric and sulphuric acids on ethyl metanitrocinnamate; it crystallizes from ether in thick, lustrous, asymmetric tablets. It behaves towards ammonia and alcohols in a similar manner to the para-compound and decomposes on boiling with water into metanitrobenzaldehyde, alcohol, nitromethane and carbon dioxide.[1]

HYDROXYPHENYLACRYLALDEHYDE,



2406 *Coumaraldehyde.* When an aqueous solution of acetaldehyde is run into a faintly alkaline solution of helicin at 50°, *glucocoumaraldehyde* is formed:



This substance crystallizes in fine needles and is decomposed by emulsin into sugar and coumaraldehyde, which forms long, fine, aromatic smelling needles, melting at 133°.

The glucocoumaraldehyde is converted by sodium amalgam and water into the corresponding alcohol, which also crystallizes in needles and yields *coumaralcohol*, $C_6H_4(OH)C_2H_2.CH_2.OH$, on treatment with emulsin. This substance is an oily liquid, which is coloured red by concentrated sulphuric acid.[2]

Tiemann and Kees endeavoured to prepare coumaraldehyde by the condensation of salicylaldehyde and acetaldehyde, but were unsuccessful. The reaction succeeds however with the nitrosalicylaldehydes, if they be brought into contact with acetaldehyde in alkaline solution.[3]

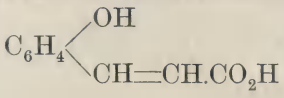
a-Nitrocoumaraldehyde, $C_6H_3(NO_2)(OH)C_3H_3O(5:2:1)$, is tolerably soluble in alcohol and almost insoluble in water, from which it crystallizes in fascicular groups of yellow needles, which melt with decomposition at 200°.

[1] Friedländer and Lazarus, *Ann. Chem. Pharm.* ccxxix. 233.
[2] Kees and Tiemann, *Ber. Deutsch. Chem. Ges.* xviii. 1955.
[3] Miller and Kinkelin, *ibid.* xx. 1931.

β-Nitrocoumaraldehyde (3 : 2 : 1) crystallizes from dilute acetic acid in lustrous, golden-yellow needles and dissolves freely in hot water to form a deep orange-coloured solution, which colours the skin brick-red; it separates on cooling in long, fine needles.

Both these aldehydes reduce ammoniacal silver solution and form phenylhydrazones.

HYDROXYPHENYLACRYLIC ACIDS,



2407 *Coumaric acid.* This acid occurs associated with coumarin, which is its anhydride, in common melilot and faham leaves.[1] Delalande and Bleibtreu obtained it by evaporating coumarin with caustic potash, and Fischer and Kuzel have prepared it from orthamidocinnamic acid by means of the diazo-reaction.[2] It is best obtained by dissolving 3·5 grm. of sodium in 60—70 cb. cm. of alcohol, adding 10 grm. of coumarin and heating for one or two hours. Water is then added, the alcohol boiled off and hydrochloric acid added. The precipitate is dissolved in a cold solution of sodium carbonate, the small quantity of coumarin which remains undissolved is removed by ether and the coumaric acid again precipitated with hydrochloric acid and finally purified by recrystallization from hot water.[3] It crystallizes in long needles, which melt at 207°—208°,[4] are slightly soluble in cold, more readily in boiling water and readily in alcohol. It may be sublimed if carefully heated, but decomposes on distillation with formation of phenol and other substances. On fusion with potash it is decomposed into salicylic and acetic acid.

Its solutions in ammonia and the alkalis show a characteristic green fluorescence.

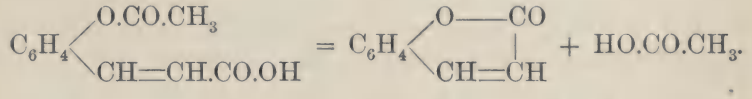
The coumarates. The metallic salts have been investigated by Zwenger. Its ethers, &c., will be described after coumarine.

Acetylcoumaric acid, $C_6H_4(OCOCH_3)C_2H_2.CO_2H$, is formed when salicylaldehyde is heated with acetic anhydride and sodium acetate, and crystallizes in needles, melting at 146°.[4]

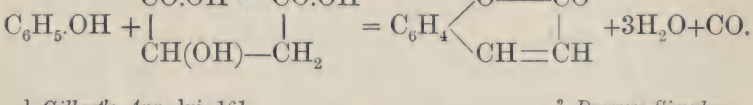
[1] Zwenger, *Ann. Chem. Pharm. Suppl.* viii. 30. [2] *Ibid.* ccxxi. 272.
[3] Fittig, *ibid.* ccxxvi. 351.
[4] Tiemann and Herzfeld, *Ber. Deutsch. Chem. Ges.* x. 284.

Coumarin, $C_9H_6O_2$. Vogel, in 1820, stated that tonka beans, the seeds of *Dipterix odorata*, a tree which is indigenous in Cayenne, and is called *coumarou* by the natives, contained benzoic acid and that he was led by the similarity of the smell of the tonka beans to that of common melilot (*Melilotus officinalis*) to discover the presence of this acid in the latter and in woodruff (*Asperula odorata*).[1] Guibort however showed that the crystalline constituent of tonka beans, is a distinct substance, which he named *coumarin*.[2] Boullay and Boutron-Challard confirmed this view,[3] and Guillemette pointed out that melilot contains the same compound,[4] which was proved by Kossmann[5] and by Bleibtreu[6] to be also present in woodruff. The latter chemist also found coumarin in the sweet-scented vernal grass (*Anthoxanthum odoratum*). In addition to these, it occurs in blue melilot (*Melilotus cæruleus*), which is employed for the preparation of herb-cheese, and in *Melilotus vulgaris*,[7] as well as in *Orchis fusca*[8] and in the pleasant-smelling leaves of *Angræcum fragrans*, an orchid which is used in Réunion as tea, under the name of *Faham*.[9] According to Rother, the husks of *Myroxylon pereiræ*, the Peru balsam-tree (Pt. IV. 20), contain 2 per cent. of coumarin.[10]

Perkin has prepared it synthetically by heating sodium salicylaldehyde with acetic anhydride,[11] and has also obtained it even more simply by boiling the aldehyde with the anhydride and sodium acetate.[12] Acetylcoumaric acid is first formed and is then decomposed on heating into acetic acid and coumarin:[13]



It is also formed in small quantities when malic acid is heated with phenol and sulphuric acid:[14]



[1] *Gilbert's Ann.* lxi. 161. [2] *Drogues Simples.*
[3] Berzelius, *Jahresb.* vii. 237; see also Delalande, *Ann. Chem. Pharm.* xlv. 332; Wöhler, *ibid.* xcviii. 66.
[4] *Ibid.* xiv. 324. [5] *Ibid.* lii. 387. [6] *Ibid.* lix. 177.
[7] Reinsch, *Jahresb. Chem.* 1867, 439. [8] Bley, *Pharm. Centralb.* 1858, 827.
[9] Gobley, *Journ. Prakt. Chem.* l. 286. [10] *Year-book Pharm.* 1885, 168.
[11] *Chem. Soc. Journ.* xxi. 53. [12] *Ber. Deutsch. Chem. Ges.* viii. 1599.
[13] Thiemer and Herzfeld, *loc. cit.* [14] v. Pechmann, *ibid.* xvii. 929.

Coumaric acid dissolves slowly in hydrobromic acid saturated at 0° and is thus converted into coumarin, which is precipitated by the addition of water after the solution has stood for some time (Fittig).

Coumarin is scarcely soluble in cold water and crystallizes from boiling water in small, rhombic plates, while it separates from ethereal solution in larger rhombic crystals, melting at 67°. According to Perkin, it boils at 290°—290·5° and its vapour has a powerful action on the brain (Delalande). Bleibtreu was unable to determine what alteration it undergoes in the animal organism, since larger doses have a narcotic action and experiments to decide the question cannot on this account be carried out. It, like coumaric acid, is converted into hydrocoumaric acid by action of sodium amalgam and water.

Coumarin is employed in perfumery, and for the manufacture of essence of woodruff. Bleibtreu says on this point: "The much-prized bouquet which distinguishes the May wine is nothing more than the aroma of this substance, and a purely scientific 'Maitrank,' prepared with coumarin, was loudly approved of by a number of students in Bonn." Rembertus Dodonæus, the celebrated botanist and physician of Maximilian II., mentions the custom of scenting wine with woodruff "to make the heart glad and the liver sound."

When one molecule of coumarin is boiled with two molecules of caustic soda, a solution is formed, which dries over sulphuric acid to a yellow, gummy mass, which is converted at 100° into a crystalline substance of the empirical formula $C_9H_6O_2(NaOH)_2$. Acids precipitate coumarin from this substance. When it is heated to 150°, the compound $C_9H_6O_2(Na_2O)$ is formed, which is not a basic sodium coumarate, since it is decomposed by acids with formation of a brown, plastic mass. Caustic potash forms a similar compound, $C_9H_6O_2(KOH)_2$, as does also baryta, the substance in this case being an amorphous deliquescent body of the formula $C_9H_6OBa(OH)_2$. Silver nitrate added to a solution of sodium coumarin, precipitates the silver compound $C_9H_6O_2(Ag_2O)$, as a canary-yellow mass, which is reconverted on heating, or by the action of nitric acid, into coumarin.[1]

If coumarin be dissolved in concentrated hydrobromic acid, the solution cooled to 0° and a current of hydrobromic acid passed

[1] Williamson, *Journ. Chem. Soc.* 1875, 850 ; see also Ebert, *Ann. Chem. Pharm.* ccxvi. 139.

through it, crystals separate out, which redissolve at the ordinary temperature. After standing for some time however, lustrous transparent crystals appear, which decompose when removed from the liquid with evolution of hydrobromic acid and fall to a powder of coumarin.[1]

2408 *Methylcoumarinic acid*, or *α-Methylcoumaric acid*, $C_6H_4(OCH_3)C_2H_2.CO_2H$, was obtained by Perkin by heating sodium coumarin with methyl iodide[2] and Ebert prepared it by heating a solution of equal molecules of coumarin, methyl iodide and sodium in methyl alcohol for several hours on the water-bath.[3] It is readily soluble in alcohol and crystallizes in monosymmetric prisms or tablets melting at 88°—89°.

Dimethyl coumarinate, $C_6H_4(OCH_3)CH_2.CO_2.CH_3$, was prepared by Perkin by employing an excess of methyl iodide. It is an oily liquid, which boils at 275°—276°.

β-Methylcoumaric acid was obtained by Perkin by heating methylsalicylaldehyde with acetic anhydride and sodium acetate, while Ebert prepared it by heating a solution of one molecule of coumaric acid, one molecule of sodium and two molecules of methyl iodide in methyl alcohol and hydrolysing the dimethyl ether which is thus formed. Perkin also found that it is formed when the *α*-acid is heated to its boiling-point, or when its concentrated alcoholic solution is exposed to sunlight, the *β*-acid commencing to crystallize out. The *β*-compound is also formed when sunlight is concentrated on the fused *α*-acid. This alteration is only brought about by the violet and ultra-violet rays.

β-Methylcoumaric acid crystallizes in small, monosymmetric prisms, which melt at 182°—183° and are tolerably soluble in alcohol.

β-Dimethyl coumarate is also formed when dimethyl coumarinate is heated, and is a strongly refractive, thick liquid boiling at 293°, the vapour of which has the sp. gr. 6·95—6·78.[4]

β-Methylcoumaramide, $C_6H_4(OCH_3)C_2H_2.CO.NH_2$, is obtained by treating the *α*- or *β*-acid with phosphorus chloride and the resulting compound with ammonia. It crystallizes from alcohol in needles, which melt at 191°—192° (Perkin).

Ethylcoumarinic acid or *α-Ethylcoumaric acid*, $C_6H_4(OC_2H_5)C_2H_2.CO_2H$, has also been investigated by Perkin and by

[1] Fittig, *Ann. Chem. Pharm.* ccxxvi. 347.
[2] *Journ. Chem. Soc.* 1877, i. 414; *ibid.* 1881, 409.
[3] *Ann. Chem. Pharm.* ccxvi. 160.
[4] Ebert, *ibid.* ccxxvi. 353.

Ebert.[1] It is only slightly soluble in hot water, from which it crystallizes in white plates, while it separates from dilute alcohol in strongly refractive tablets, melting at 103°—104°.

Calcium ethylcoumarinate, $(C_{11}H_{11}O_3)_2Ca + 2H_2O$, crystallizes from hot water in radiating groups of lustrous needles.

Ethyl ethylcoumarinate, $C_6H_4(OC_2H_5)C_2H_2.CO_2C_2H_5$, is a liquid, which boils at 290°—291°.

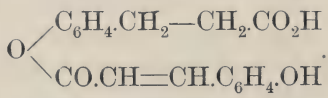
β-Ethylcoumaric acid has been obtained by Perkin from ethylsalicylaldehyde and by Ebert from coumaric acid. It is also formed when the *α*-acid is heated and crystallizes from hot water in fine, lustrous needles and from alcohol in small prisms, melting at 135°.

Calcium ethylcoumarate, $(C_{11}H_{11}O_3)_2Ca + 2H_2O$, crystallizes in large, hard needles and is much less soluble than ethyl cumarinate.

Ethyl ethylcumarate is an oily liquid, which boils at 302°—304°.

The cause of the relations between the substituted coumarinic and coumaric acids is probably to be sought for in geometrical isomerism (p. 237). The chemical properties of both are identical; thus the two ethylated acids yield ethylsalicylaldehyde on oxidation and are reduced to ethylmelilotic acid by sodium amalgam and water (p. 173). If solutions of ethylcoumarinic acid and bromine in carbon disulphide be mixed, *ethoxyphenyldibromopropionic acid*, $C_6H_4(OC_2H_5)CHBr.CHBr.CO_2H$, is formed in small crystals, which melt with decomposition at 155°. The same acid is also obtained from ethylcoumaric acid, which however combines much more slowly with bromine. The methylated acids behave in a precisely similar manner. The brominated compounds are converted by alcoholic potash into substituted phenylbromacrylic acids.

Coumarin-melilotic acid, $C_{18}H_{16}O_5$. According to Zwenger and Bodenberger, melilot does not contain free coumarin but this compound. It crystallizes in tablets, which are scarcely soluble in water but dissolve readily in alcohol and ether melts at 128° and is resolved into its components by ammonia.[2] Its constitution can be expressed by the following formula :[3]



[1] *Ann. Chem. Pharm.* ccxxvi. 139.
[2] *Ann. Chem. Pharm.* cxxvi. 257.
[3] Schiff, *Ber. Deutsch. Chem. Ges.* v. 665.

Thiocoumarin, $C_6H_4\left\langle\begin{array}{l}CH{=}CH\\ \quad\quad\;\; |\\ O\text{---}CS\end{array}\right.$, is formed when coumarin is heated with phosphorus pentasulphide, and crystallizes from alcohol in long, golden-yellow needles, which melt at 101°, sublime when more strongly heated and do not possess a characteristic odour. It is reconverted into coumarin by heating with caustic potash.

Coumaroxime, $C_6H_4\left\langle\begin{array}{l}CH{=}CH\\ \quad\quad\;\; |\\ O\text{---}C{=}N.OH\end{array}\right.$, is obtained by the action of hydroxylamine on an alcoholic solution of thiocoumarin, while coumarin itself does not react with hydroxylamin. It crystallizes from boiling water in long, white needles, which melt at 131° and are decomposed by heating with hydrochloric acid into coumarin and hydroxylamine. When it is heated with sodium ethylate and ethyl iodide, *coumaroxime ethyl ether*, $C_6H_4.C_3H_2O(NOC_2H_5)$, is formed; it crystallizes from alcohol in plates, which melt at 50°. If coumaroxime be treated with sodium amalgam and water, it is converted into *hydrocoumaroxime*, $C_6H_4.C_3H_4O(NOH)$, which is readily soluble in water and alcohol and is decomposed into hydroxylamine and melilotic anhydride by heating with hydrochloric acid:

$$C_6H_4\left\langle\begin{array}{l}CH_2\text{—}CH_2\\ \quad\quad\;\; |\\ O\text{——}C{=}N.OH\end{array}\right. + H_2O = C_6H_4\left\langle\begin{array}{l}CH_2\text{—}CH_2\\ \quad\quad\;\; |\\ O\text{——}CO\end{array}\right. + H_2N.OH.$$

Coumarinphenylhydrazone, $C_6H_4\left\langle\begin{array}{l}CH{=}CH\\ \quad\quad\;\; |\\ O\text{---}C{=}N - NHC_6H_5\end{array}\right.$, is formed when thiocoumarin and phenylhydrazine are heated together in alcoholic solution, and crystallizes from alcohol in long, golden-yellow needles, melting at 143°—144°.[1]

2409 *Substitution products of coumarin.* When chlorine is passed into a solution of coumarin in chloroform, the dichloride, $C_9H_6Cl_2O_2$, is formed as a thick, syrupy liquid, which is decomposed by heat, or by the action of alcoholic potash, into the following compound.

a-Chlorocoumarin, $C_6H_4.C_3HClO_2$, is also formed when coumarin is heated to 200° with phosphorus pentachloride, and crystallizes from alcohol in long needles, which melt at 122°—123°.[2]

[1] Tiemann, *Ber. Deutsch. Chem. Ges.* xix 1661.
[2] Perkin, *Zeitschr. Chem.* 1871, 178.

β-Chlorocoumarin, $C_6H_3.Cl.C_3H_2O_2$, is obtained by heating the sodium compound of chlorosalicylaldehyde with acetic anhydride and is a crystalline substance, melting at 162°.[1]

α-Bromocoumarin, $C_6H_4.C_3HBrO_2$. Coumarin combines with bromine to form the dibromide, $C_6H_4.C_3H_2Br_2O_2$, which crystallizes from alcohol in oblique prisms and from carbon disulphide in large prisms, melting at 105°.[2] It is converted by alcoholic potash into bromocumarin, which forms prisms melting at 110°.

β-Bromocoumarin, $C_6H_3Br.C_3H_2O$, has been prepared from bromosalicylaldehyde by Perkin. It is also formed, together with free coumarin and *α*-dibromocoumarin, when coumarin dibromide is heated; this last substance decomposes into coumarin and bromine, which then exerts a substituting action.[3] *β*-Bromocoumarin crystallizes from alcohol in flat prisms, melting at 160°.

α-Dibromocoumarin, $C_6H_3Br.C_3HBrO_2$, was obtained by Perkin by heating coumarin with bromine containing iodine;[4] it crystallizes from boiling alcohol in small needles, which melt at 179° (Fittig).

β-Dibromocoumarin, $C_6H_2Br_2.C_3H_2O_2$, was prepared by Perkin from dibromosalicylaldehyde. It is also formed when a solution of coumaric acid and bromine in carbon disulphide is allowed to stand. An addition product is formed and decomposes in the air into hydrobromic acid and dibromocumarin (Fittig). The latter crystallizes from alcohol in small, lustrous needles, melting at 177°.

Nitrocoumarin, $C_9H_5(NO_2)O_2$, is formed by dissolving coumarin in fuming nitric acid, and by heating *α*-nitrosalicylaldehyde with sodium acetate.[5] It crystallizes in fine needles, which melt at 183° and form a deep-yellow solution in alkalis (Delalande, Bleibtreu).

Amidocoumarin, $C_9H_5(NH_2)O_2$, is obtained by reducing nitrocoumarin with iron filings and acetic acid, and crystallizes in long needles, melting at 168°—170°.[6]

Coumarilic acid, $C_9H_6O_3$, has been prepared by Perkin by heating *α*-chlorocoumarin and *α*-bromocoumarin with alcoholic potash. It is best obtained by bringing coumarin dibromide

[1] Bäsecke, *Ann. Chem. Pharm.* cliv. 85.
[2] Fittig and Ebert, *ibid.* ccxvi. 163.
[3] Fittig, *Ann. Chem. Pharm.* ccxxvi. 347.
[4] Perkin, *ibid.* clvii. 117.
[5] Taege, *Ber. Deutsch. Chem. Ges.* xx. 2109.
[6] Frapolli and Chiozza, *Ann. Chem. Pharm.* xcv. 253.

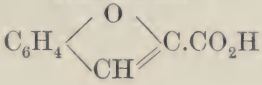
into hot alcoholic potash and then heating for a short time.[1] It crystallizes from hot dilute alcohol in needles, melting at 190°—191° and boils almost without decomposition at 310°—315°. It does not combine with bromine or hydrobromic acid and is decomposed into acetic and salicylic acids by fusion with potash. It is a monobasic acid and forms crystalline salts.

Hydrocoumarilic acid, $C_9H_8O_3$, is formed by the action of sodium amalgam and water on coumarilic acid, and is more readily soluble in water than the latter, crystallizing in nacreous plates, which melt at 116·5°. It boils with partial decomposition at 298·5°—300·5°, a small quantity of phenol being formed. Its salts crystallize well; the ethyl ether only dissolves slowly in caustic soda and is simultaneously saponified.

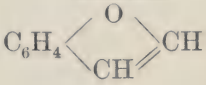
Coumaron, C_8H_6O, is obtained by the distillation of coumarilic acid with lime, and by heating aldehydophenoxyacetic acid (Pt. IV. p. 289), with acetic anhydride and sodium acetate.[2] It is an oily liquid, which boils at 168·5°—169·5°, is insoluble in alkalis and combines with bromine to form *coumaron dibromide*, $C_8H_6OBr_2$, which crystallizes from carbon disulphide in large, colourless prisms, melting at 86°. This substance is converted by the action of hot alcoholic potash into *bromocoumaron*, C_8H_5BrO, which crystallizes from dilute alcohol in needles, melting at 36°, volatilizes at the ordinary temperature and has a strong odour.[3]

The following formulæ express the most probable constitution, of these substances:

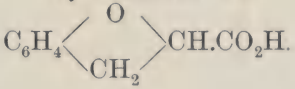
Coumarilic acid.



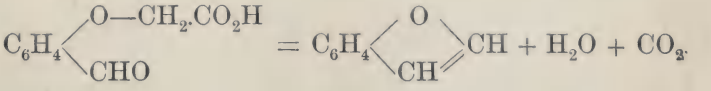
Coumaron.



Hydrocoumarilic acid.



The formation of coumaron from aldehydophenoxyacetic acid would then take place as follows:



[1] Fittig and Ebert, *Ann. Chem. Pharm.* ccxvi. 162.
[2] Rössing, *Ber. Deutsch. Chem. Ges.* xvii. 3000.
[3] Ebert, *Ann. Chem. Pharm.* ccxxvi. 354.

2410 *Paracoumaric acid*, $C_6H_5.C_2H_2.CO_2H$. This compound was obtained by Hlasiwetz by boiling aloes with dilute sulphuric acid, a yield of 1—1·5 per cent. being given.[1] It may be synthetically prepared by heating parahydroxybenzaldehyde with anhydrous sodium acetate and acetic anhydride to 175° in a sealed tube.[2] It crystallizes from hot water in needles, melting at 206° (Tiemann and Herzfeld); its alcoholic solution is coloured dark golden-brown by ferric chloride. On fusion with caustic soda or potash, it is decomposed into parahydroxybenzoic acid and acetic acid.[3] It is reduced to hydroparacoumaric acid by nascent hydrogen.

Methylparacoumaric acid, $C_6H_4(OCH_3)C_2H_2.CO_2H$, has been prepared by Perkin by heating anisaldehyde with acetic anhydride and sodium acetate, the method described under paracoumaric acid being followed (Eigel). It crystallizes from alcohol in faintly yellow needles, melting at 171°.[4] It is also formed when sodium phenylglycolate is heated with anisaldehyde and acetic anhydride, *methylphenoxyparacoumaric acid*, $(CH_3O)C_6H_4.CH{=}C.(OC_6H_5)CO_2H$, being simultaneously obtained; the latter crystallizes from alcohol in rectangular tablets, melting at 200°.[5]

Methylparacoumaryl chloride, $C_6H_4(OCH_3)C_2H_2.COCl$, is a crystalline mass, which melts at 50° and is converted by ammonia into the amide, $C_6H_4(OCH_3)C_2H_2.CONH_2$, which separates from alcohol in scales, melting at 186°.

Methyl methylparacoumarate, $C_6H_4(OCH_3)C_2H_2.CO_2.CH_3$, is formed by the action of the chloride on methyl alcohol, crystallizes in large tablets, melts at 89° and boils at 303.°[6]

Ethyl methylparacoumarate, $C_6H_4(OCH_3)C_2H_2.CO_2C_2H_5$, occurs in the root of *Hedychim spicatum*, a plant related to the ginger, which is used in India as a perfume under the name of Kafurkachri. A pleasant smelling oil and the above acid are extracted by petroleum-spirit, the latter crystallizing in tablets, which melt at 49° and are decomposed by caustic potash into alcohol and methylparacoumaric acid.[7]

Acetylparacoumaric, $C_6H_4(O.COCH_3)C_2H_2.CO_2H$, is formed when the sodium compound of parahydroxybenzaldehyde is heated with acetic anhydride and sodium acetate. It crystal-

[1] *Ann. Chem. Pharm.* cxxxvi. 31; Eigel, *Ber. Deutsch. Chem. Ges.* xx. 2527.
[2] Tiemann and Herzfeld, *ibid.* x. 65; Eigel, *loc. cit.*
[3] Barth and Senhofer, *ibid.* xii. 1259. [4] *Journ. Chem. Soc.* 1877, i. 408.
[5] Valentini, *Gaz. Chim. Ital.* xiv. 147. [6] Perkin, *ibid.* 1881, i. 439.
[7] Thresh, *Pharm. Journ. Trans.* [3] xv. 361.

lizes from hot water in fine, matted needles, which melt at about 195°, but commence to sublime at a lower temperature. On heating with caustic potash it decomposes into acetic and paracoumaric acids.[1]

Naringin, $C_{21}H_{26}O_{11} + 4H_2O$, was discovered by De Vry in the flowers and almost all the parts of *Citrus decumana*, and was mistaken by him for hesperidin (p. 251). Its name is derived from *naringi* (Sanscrit: orange). It has a bitter taste, is slightly soluble in cold, almost in every proportion in hot water and crystallizes in colourless, microscopic prisms, which lose water on heating and melt at 170°—171°. It forms a yellowish-red solution in alkalis and is reprecipitated by carbon dioxide. On heating with dilute sulphuric acid, it is decomposed into grape sugar, isodulcite and *naringenin*, $C_{15}H_{12}O_5$, which is insoluble in water and crystallizes from dilute alcohol in lustrous, tasteless needles, which dissolve readily in caustic potash and are decomposed when this solution is heated into phloroglucinol and paracoumaric acid.[2] Its constitution is therefore probably expressed by the following formula:

$$HO.C_6H_4.CH{=}CH.CO.OC_6H_3(OH)_2.$$

DIHYDROXYPHENYLACRYLIC ACIDS,

$$C_6H_3\begin{cases}OH\\OH\\CH{=}CH.CO_2H.\end{cases}$$

2411 *Caffeïc acid* (1 : 2 : 4). A characteristic compound which is called *caffeetannic acid*, $C_{15}H_{18}O_8$ and forms a gummy mass, is contained in coffee beans[3] and the caïnca-root (*Chiococca racemosa*).[4] On boiling with caustic potash, it decomposes into a sugar-like substance, $C_6H_{10}O_4$, and caffeïc acid,[5] which has also been prepared synthetically from protocatechualdehyde and acetic anhydride.

[1] Tiemann and Herzfeld, *Pharm. Journ. Trans.* [3] xv. 361.
[2] Will, *Ber. Deutsch. Chem. Ges.* xviii. 1311; xx. 294 and 1186.
[3] Pfaff, *Schweiger's Journ.* lxii. 31; Rochleder, *Ann. Chem. Pharm.* lix. 300, lxvi. 35.
[4] Rochleder and Hlasiwetz, *Jahresber. Chem.* 1850, 387.
[5] Hlasiwetz, *Ann. Chem. Pharm.* cxlii. 221.

In order to prepare it, 50 grms. of commercial coffee extract (*Extract. coffeæ alc.*), prepared by means of alcohol, are boiled with 100 grms. of water and 50 grms. of caustic potash for one hour, diluted with 200 grms. of water, acidified with sulphuric acid and repeatedly extracted with ether. The acid left after the evaporation of the ether is boiled up with animal charcoal and crystallized from water. The yield amounts to 6—7 grms.[1]

Caffeïc acid crystallizes in small, straw-yellow, lustrous prisms or plates and its aqueous solution is coloured grass-green by ferric chloride; the addition of sodium carbonate converts the colour into blue and finally into reddish-violet. The acid is reduced to hydrocaffeïc acid by sodium amalgam and water; on distillation with potash it yields protocatechuic acid, while pyro-catechol is formed on dry distillation.

Metamethylcaffeïc acid, $C_6H_3(OH)(OCH_3)C_2H_2.CO_2H(1:2:4)$, was discovered by Barth and Hlasiwetz in *Asa fœtida*, the resin of various species of Ferula or Narthesium and is called *ferulaïc acid*.[2] Tiemann and Nagai then prepared it synthetically from vanillin. It crystallizes in four-sided, rhombic needles, which melt at 168°—169° and are scarcely soluble in water, but dissolve more readily in boiling water and readily in alcohol. It is reduced to hydroferulic acid by sodium amalgam and water.

Ferulaldehyde, $C_6H_3(OH)(OCH_3)C_2H_2.CHO$. When glucovanillin (Pt. IV. p. 347) is acted upon by acetaldehyde and caustic soda, *glucoferulaldehyde*, $C_6H_3(OC_6H_{11}O_5)(OCH_3)C_2H_2.CHO + 2H_2O$, is formed, which crystallizes from hot water in light yellow needles, melting at 200°—202°. Its aqueous solution is laevorotatory, and colours a solution of fuchsin-sulphurous acid red. Emulsin resolves it into dextrose and ferulaldehyde, which is readily soluble in alcohol and benzene and is precipitated by petroleum-spirit from solution in the latter in light yellow needles, which melt at 84° and have a faint aromatic odour. Its solution is coloured bluish-green by ferric chloride, vanillin being formed if the mixture be heated.[3]

Paramethylcaffeïc acid, (2 : 1 : 4), was prepared by Tiemann and Nagai by heating caffeïc acid with methyl iodide, caustic potash and wood-spirit, and was called isoferulic acid.[4] Tiemann and Will then discovered that it is identical with hesperetic acid, a decomposition product of hesperidin.[5] It crystallizes in needles,

[1] *Ann. Chem. Pharm.* cxlii. 357.
[2] *Ibid.* cxxxviii. 64.
[3] Tiemann, *Ber. Deutsch. Chem. Ges.* xviii. 3482.
[4] *Ibid.* xi. 646.
[5] Hoffmann, *ibid.* ix. 685; x. 686; Tiemann and Will, *ibid.* xiv. 946.

which are slightly soluble in cold, more readily in hot water and alcohol and melt at 228°; it decomposes into carbon dioxide and hesperetol when its calcium salt is distilled (p. 32). Its alkali salts are colourless, while those of ferulaïc acid have a yellowish colour.

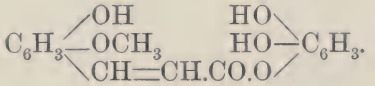
	Melting-point.
Dimethylcaffeïc acid, $C_6H_3(OCH_3)_2C_2H_2.CO_2H$ lustrous needles	180°—181°
Methyldemethylcaffeate, $C_6H_3(OCH_3)_2C_2H_2.CO_2.CH_3$, pointed prisms	64°

Acetylferulic acid, $C_6H_3(O.CO.CH_3)(OCH_3)C_2H_2.CO_2H$, is formed by boiling vanillin with acetic anhydride and sodium acetate, and crystallizes from alcohol in fine needles, melting at 196°—197°. On heating with caustic potash it decomposes into acetic acid and ferulic acid (Tiemann and Nagai).

Acetylisoferulic acid is obtained by heating isoferulic acid with acetic anhydride and crystallizes from alcohol in plates, melting at 199° (Tiemann and Will).

Diacetylcaffeïc acid, $C_6H_3(O.CO.CH_3)C_2H_2.CO_2H$, is formed when caffeïc acid is heated with acetic anhydride and when protocatechualdehyde is heated with sodium acetate and acetic anhydride. It crystallizes from dilute alcohol in fine needles, melting at 190°—191°. On heating with caustic potash it decomposes into acetic acid and caffeïc acid (Tiemann and Nagai).

2412 *Hesperetin*, $C_{16}H_{14}O_3$, is obtained when hesperidin is heated to 115°—120° for three hours with 5 or 6 parts of 50 per cent. alcohol, which contains 2 per cent. of sulphuric acid. It crystallizes from dilute alcohol in small plates with a satin lustre and from boiling water in flat, rectangular tablets, which are very slightly soluble in cold water, have a very sweet taste and melt at 226° with partial carbonization and decomposition. It dissolves readily in alkalis but is reprecipitated by carbon dioxide; when boiled with caustic potash it decomposes into isoferulic acid and phloroglucinol. It has therefore the following constitution (Tiemann and Will):

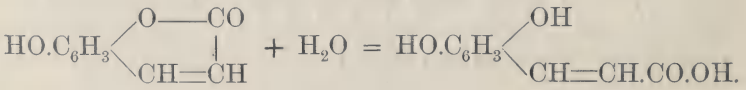


Hesperidin, $C_{22}H_{26}O_{12}$. This name was given by Lebreton to a crystalline body, which occurs in the fruits, and especially

the pulp and skin, of some species of the Aurantiaceæ.[1] It thus occurs in *Citrus limonum*, *C. medica*, *C. aurantium*, *C. chinensis*, *C. longifolia*, *C. mandarin*, and *C. curassaviensis*,[2] and also in their leaves, while it is not found in *C. vulgaris*, *C. bigaradia*, *C. decumana* (Pfeffer). It is best obtained from the officinal, dried unripe orange (*Fructus aurantii immaturi*) by washing the roughly powdered fruit with cold water, as long as the filtrate gives a precipitate with lead acetate. The residue is then extracted with 50 per cent. alcohol, to which 2 per cent. of caustic soda has been added, until the solution is no longer coloured. Hydrochloric acid is then added, the precipitate extracted with boiling 90 per cent. alcohol to remove coloured impurities and the residue dissolved in weak caustic potash, a little alcohol being then added and the product finally reprecipitated by carbon dioxide.[3]

Hesperidin forms an odourless and tasteless mass consisting of microscopic needles, which are very hygroscopic, but are scarcely soluble in water, only slightly in alcohol and insoluble in ether; it may be obtained from boiling glacial acetic acid in larger needles. It readily dissolves in alkalis, as mentioned above; when it is heated for a few minutes with sodium amalgam and water, an orange-coloured solution is formed, in which hydrochloric acid produces a precipitate, which forms a magenta-red solution in alcohol. This substance, which has also been obtained from naringin, has not been further investigated. It may probably be related to the colouring matter of orange-peel, Berzelius having observed that this substance contains much hesperidin.[4] The latter decomposes on heating with dilute acids in a similar manner to naringin, into grape-sugar, isodulcite and hesperitin.[5]

2413 *Umbellic acid* (1 : 3 : 4). This name was formerly applied to hydro-umbellic acid, the compound in question being called umbelliferonic acid, since it is formed when umbelliferon is heated with dilute caustic potash:[6]



[1] *Journ. Pharm.* 1828, xiv. 377.
[2] Pfeffer, *Ber. Deutsch. Chem. Ges.* ix. 27; Paterno and Briosi, *ibid.* ix. 250; Tschirch, *ibid.* xiv. 948.
[3] Hoffmann, *ibid.* ix. 690; Tiemann and Will, *ibid.* xiv. 946.
[4] Berzelius, *Jahresber.* xxxii. 451.
[5] Will, *Ber. Deutsch. Chem. Ges.* xx. 1186.
[6] Reimer and Tiemann, *ibid.* xii. 993; Posen, *ibid.* xiv. 2744.

It forms a yellowish powder, which is readily soluble in alcohol and hot water and becomes converted into a resinous mass on continued boiling with water.

Umbelliferon, $C_9H_6O_3$, is formed by the distillation of the resins of various Umbelliferæ,[1] such as that of the sumbul root (*Euryangium sumbul*), Asafœtida and especially that of the galtree, both of which are derived from species of Ferulaceæ. It is also obtained from the alcoholic extract of *Daphne mezereum*[2] and may be synthetically prepared by heating resorcinol and malic acid with sulphuric acid, the reaction corresponding to the formation of coumarin from malic acid and phenol.[3]

It is almost insoluble in cold water, dissolves in 100 parts of boiling water and crystallizes on cooling in fine needles, which melt at 223°—224° and smell like coumarin when heated. It dissolves in concentrated sulphuric acid without decomposition, forming a solution which shows a dark blue fluorescence. Water and sodium amalgam convert it into hydro-umbellic acid. On fusion with potash, β-resorcylic acid (Pt. IV. p. 359) is formed.

Methylumbelliferon, $C_9H_5(OCH_3)O_2$, is formed when umbelliferon is heated with methyl iodide, caustic potash and wood-spirit. It crystallizes in plates, which have a strong odour of coumarin when heated, and melts at 114° (Tiemann and Reimer).

It yields two isomeric dimethylumbellic acids, behaving in this respect in an analogous manner to methylcoumarin.

α-Dimethylumbellic acid, $C_6H_3(OCH_3)_2C_2H_2.CO_2H$, is obtained by heating a solution of methylumbelliferon and equal molecules of methyl iodide and sodium in wood-spirit, the methyl ether being then hydrolyzed. It crystallizes from alcohol in needles, melting at 138°, and is converted into the following compound when it is heated to the boiling-point.

β-Dimethylumbellic acid is also obtained by evaporating methylumbelliferon with caustic soda, heating the residue with methyl iodide and wood-spirit and hydrolysing the ether which is thus obtained. It crystallizes from hot water in lustrous needles, melting at 180°—181°.

Both these acids are converted by sodium amalgam and water into *dimethoxyphenylpropionic acid*, melting at 105°, and yield the same dimethyl-β-resorcylic acid on oxidation[4]

[1] Sommer, *Jahresb. Chem.* 1859, 573; Hlasiwetz and Grabowski, *Ann. Chem. Pharm.* cxxxix. 100. [2] Zwenger, *Ann. Chem. Pharm.* cxv. 15.
[3] von Pechmann, *Ber. Deutsch. Chem. Ges.* xvii. 929.
[4] Tiemann and Will, *ibid.* xv. 2080; Will, *ibid.* xvi. 2115; Will and Beck, *ibid.* xix. 1777.

Acetylumbelliferon, $C_9H_5(O.CO.CH_3)O_2$, is obtained by heating umbelliferon with acetic anhydride or acetyl chloride,[1] or resorcylaldehyde with sodium acetate and acetic anhydride.[2] It crystallizes from hot water in large prisms, melting at 140° and its aqueous solution shows a blue fluorescence.

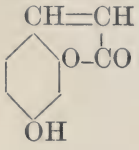
Metahydroxycoumarin, $C_9H_6O_2$, is prepared by the action of sulphuric acid on a mixture of malic acid and quinol and crystallizes from boiling water in needles which melt at 248°—250°. Its solution does not show any fluorescence.[3]

Metamethoxycoumarin, $C_9H_5(OCH_3)O_2$, is the methyl ether of the preceding compound, and is obtained by boiling methoxysalicyl aldehyde with acetic anhydride and sodium acetate. It forms tabular plates, which melt at 103° and smell like coumarin.[4]

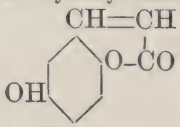
Orthohydroxycoumarin, $C_9H_6O_2$, has been prepared from catechol and malic acid; it crystallizes from alcohol in fine needles, which melt with decomposition at 280°—285°.[5]

The constitution of the hydroxycoumarins is expressed by the following formulæ:

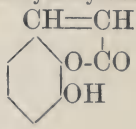
Umbelliferon.



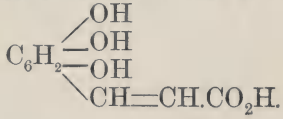
Metahydroxycoumarin.



Orthohydroxycoumarin.



TRIHYDROXYPHENYLACRYLIC ACIDS,

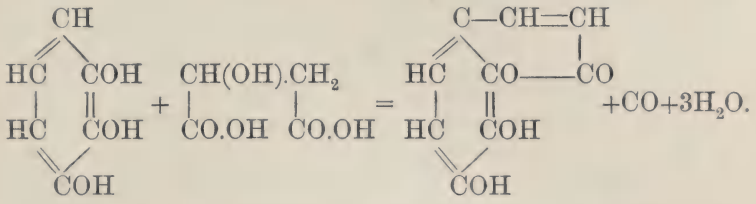


2414 Only the substituted derivatives of these compounds, and the anhydrides, the dihydroxycoumarins, are known.

Daphnetin, $C_9H_6O_4$. The glucoside of this substance, daphnin, occurs in the bark of many species of *Daphne*, *D. alpina*, *D. mezereum* [6] and is decomposed on boiling with dilute acids or by

[1] Hlasiwetz, *ibid.* iv. 450; Tiemann and Reimer, *ibid. loc. cit.*
[2] Tiemann and Lenz, *ibid.* x. 2216.
[3] Pechmann and Welsch, *ibid.* xvii. 1646.
[4] Tiemann and Müller, *Ber. Deutsch. Chem. Ges.* xiv. 1996.
[5] Bizzari, *ibid.* xviii. Ref. 333.
[6] Vauquelin, *Ann. Chim. Phys.* lxxxiv. 173; Baer and Gmelin, *Schweigg. Journ.* xxxv. 1.

the action of emulsin into glucose and daphnetin.[1] Its correct composition was determined by Rochleder[2] and its constitution has been ascertained by v. Pechmann[3] and by Will and Jung.[4] The former obtained it synthetically by heating pyrogallol and malic acid with sulphuric acid:



It crystallizes from hot water in yellowish needles or prisms, which melt at 255°—256° and smell like coumarin on heating. Its aqueous solution is coloured green by ferric chloride, the colour being changed to red by sodium carbonate. If it be dissolved in a boiling solution of acid sodium sulphite and ammonia, and potassium ferricyanide added, a reddish yellow colouration is produced, while if ferric chloride be added to the bisulphite solution it is coloured deep blue.[5] Its reddish yellow alkaline solution decomposes on standing or boiling. When daphnetin is heated with methyl iodide, caustic potash and alcohol, the following two compounds are formed:

Mono-ethyldaphnetin, $C_9H_5(OC_2H_5)O_3$, crystallizes from dilute alcohol in lustrous plates, which melt at 155° and are soluble in alkalis.

Diethyldaphnetin, $C_9H_4(OC_2H_5)_2O_2$, crystallizes from alcohol in needles melting at 72°, which dissolve slowly in a hot alkaline solution with a yellow colour and are reprecipitated by acids. Bromine converts it into diethylmonobromodaphnetin, which is converted by boiling with alkalis into *diethyldaphnetilic acid*, $C_9H_4(OC_2H_5)_2O_3$, which corresponds to coumarilic acid and forms crystals which resemble asbestos, and melt at 154°.

Triethyldaphnetic acid, $C_6H_2(OC_2H_5)_3C_2H_2CO_2H$, is formed when an alkaline solution of diethyldaphnetin is evaporated and the residue heated with alcohol and ethyl iodide. The ethyl ether is thus formed, and is then hydrolysed by alcoholic

[1] Zwenger, *Ann. Chem. Pharm.* cxv. 1.
[2] *Jahresb.* 1863, 592.
[3] *Ber. Deutsch. Chem. Ges.* xvii. 929.
[4] *Ibid.* xvii. 1081.
[5] v. Pechmann and Cohen, *ibid.* xvii. 2189.

potash. The acid forms crystals, melting at 193°. It is converted by water and sodium amalgam into *triethylhydrodaphnetic acid*, $C_6H_2(OC_2H_5)_3C_2H_4CO_2H$, which forms crystals, melting at 85°.

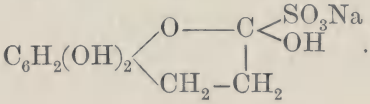
Triethyldaphnetic acid is converted into triethylpyrogallocarboxylic acid (Pt. IV. p. 378) by the action of potassium permanganate (Will and Jung).

Diacetyldaphnetin, $C_9H_4(OCOCH_3)_2O_2$, crystallizes from dilute alcohol in needles, which melt at 128°—129° (von Pechmann).

Daphnin, $C_6H_2(OC_6H_{11}O_5)OH(C_3H_2O_2) + 2H_2O$, crystallizes from hot water in rectangular, prisms which become anhydrous at 100° and form a yellow solution in alkalis.

2415 *Æsculetin*, $C_9H_6O_4 + H_2O$, occurs in small quantity in the bark of the horse-chestnut (*Æsculus hippocastanum*),[1] accompanied by its glucoside, æsculin, from which it can be readily obtained by decomposition with acids or emulsin.[2]

It crystallizes from boiling water in very fine, lustrous needles, which lose water and become yellow at 100°. On heating it smells like coumarin and melts with decomposition at 270°. Its yellow aqueous solution has a faint blue fluorescence and is coloured deep green by ferric chloride; it forms a yellow solution in alkalis. It combines with acid sodium sulphite to form the compound $C_9H_8O_4 + NaHSO_3$,[3] which probably has the following constitution:



It crystallizes in small needles with a satin lustre and forms a solution, which becomes red when heated with ammonia and exposed to the air, the colour changing to azure blue and finally to blood-red, a splendid fluorescence being also produced.

When the sulphite compound is decomposed by sulphuric acid, *hydro-æsculetin*, $C_9H_8O_4$, is obtained. This compound was named *paræsculetin* by Rochleder, who considered it to be isomeric with æsculetin. It is readily soluble in water, crystallizes badly and also gives a blue colouring matter with ammonia, a solution of which dries to an amorphous mass possessing a splendid violet metallic lustre. The solution of the original compound alters on standing and yields a brown mass with a

[1] Rochleder, *Jahresb. Chem.* 1863, 589.
[2] Rochleder and Schwarz, *Ann. Chem. Pharm.* lxxxviii. 356.
[3] Rochleder, *loc. cit.*; Liebermann and Knietsch, *Ber. Deutsch. Chem. Ges.* xiii. 1591.

faint green lustre on evaporation; traces of alcohol colour the solution pink and impart to it a splendid cinnabar-red fluorescence, this reaction being so delicate that distilled water can thus be distinguished from spring water containing calcium carbonate.[1]

Methylæsculetin, $C_9H_5(OCH_3)O_3$, is formed, together with following compound, when æsculetin is heated with a solution of caustic potash and methyl iodide in wood-spirit and crystallizes in lustrous needles, which melt at 184° and dissolve in alkalis to form a solution showing a green fluorescence.

Dimethylæsculetin, $C_9H_4(OCH_3)_2O_2$, crystallizes from hot water in lustrous needles, melting at 144°.

The following compounds have been obtained in a similar manner:

Ethylæsculetin, $C_9H_5(OC_2H_5)O_3$, forms colourless or yellowish crystals, which melt at 143°; its alcoholic solution shows a blue fluorescence.

Diethylæsculetin, $C_9H_4(OC_2H_5)_2O_2$, crystallizes in silvery plates, melting at 109°. It is converted by bromine into *diethylmonobromæsculetin*, which crystallizes in lustrous needles, melting at 169°, and on heating with alcoholic potash yields *diethoxycoumarilic acid*, $C_{13}H_{14}O_5$, a substance which forms fine needles and melts at 195°.

α-Triethylæsculetic acid, $C_6H_2(OC_2H_5)_3C_2H_2CO_2H$, is formed when diethylæsculetin and equal molecules of ethyl iodide and sodium are dissolved in absolute alcohol and heated on the water-bath for four or five hours. The ethyl ether thus obtained, which crystallizes in thick yellow prisms, melting at 51°, is hydrolyzed with alcoholic potash. The free acid forms crystals, which melt at 102°—103°; when it or its ether is heated to the boiling-point, the following isomeric compounds are formed.

β-Triethylæsculetic acid. The ether of this acid is also formed by using a slight excess of ethyl iodide in the above method and heating for eight hours. It crystallizes in lustrous tablets, melting at 75°; the acid forms silvery crystals, melting at 144°.

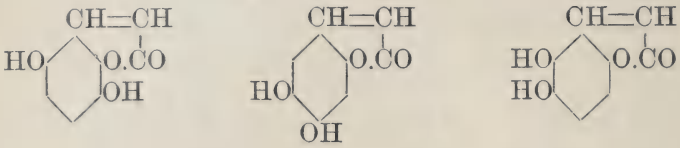
Both acids are converted by sodium amalgam and water into triethoxyphenyl-propionic acid, $C_6H_2(OC_2H_5)_3C_2H_4CO_2H$, and on oxidation yield a triethoxybenzoic acid, $C_6H_2(OC_2H_5)_3CO_2H$, which decomposes on heating with lime into carbon dioxide and hydroxyquinol triethyl ether.[2]

[1] Liebermann and Mastbaum, *ibid.* xiv. 474.

[2] Will, *Ber. Deutsch. Chem. Ges.* xvi. 2106; Will and Albrecht, *ibid.* xvii. 2108; Will and Pukali, *ibid.* xx. 1119.

Diacetylæsculetin, $C_9H_4(O.CO.CH_3)_2O_2$, crystallizes from alcohol in prisms, melting at 133°—134° (Liebermann and Mastbaum).

The constitution of æsculetin has not yet been determined with certainty, since the position of the acrylic acid residue is still unknown; it must however be represented by one of the following three formulæ:



Æsculin, $C_6H_2(OH)(OC_6H_{11}O_5)C_3H_2O_2$. The apothecary Frischmann was the first to observe that the yellow-coloured extract of the skin of horse-chestnuts shows a blue reflection [1] and Remmler prepared the compound which gives it this property in a tolerably pure condition.[2] Raab, another apothecary, then re-discovered it and named it *schillerstoff*,[3] while Martius gave it the name of *bicolorin* and Kastner termed it *polychrom*;[4] Berzelius then proposed the name æsculinic acid, which was finally changed into æsculin. According to Jonas, it is found in the bark in largest quantity in spring before the buds are open,[5] and also occurs in the root bark of the American wild jasmine (*Gelsemium sempervirens*).[6]

In order to prepare it, horse-chestnut bark is extracted with boiling water, the solution precipitated with lead acetate, the filtrate heated with sulphuretted hydrogen, again filtered and evaporated. The æsculin separates out and is purified by recrystallization from alcohol and water.[7] The bark may also be extracted with dilute ammonia, the solution evaporated and the residue mixed with alumina and extracted with 95 per cent. alcohol. The æsculin, which crystallizes out, is shaken up with water and ether and then washed with benzene.[8]

Properties.—It forms small prisms, containing $1\frac{1}{2}$ molecules of water, which is lost at 120°—130°; it melts at 160° with decom-

[1] *Crell's Chem. Journ.* v. 5.
[2] "Ueber die Doppelfarbe der wilden Kastanienrinde"; *Taschenbuch. f. Scheidekunde und Apoth.* 1785.
[3] *Archiv für Naturkunde*, x. 121.
[4] *Ann. Chem. Pharm.* xiv. 190.
[5] *Ibid.* xv. 266.
[6] Sonnenschein, *Ber. Deutsch. Chem. Ges.* ix. 1182.
[7] Rochleder and Schwarz, *Ann. Chem. Pharm.* lxxxvii. 186.
[8] Fairthorne, *Jahresber. Chem.* 1872, 788.

position[1] and decomposes at 230° into æsculetin and glucosan.[2] It dissolves, according to Trommsdorff, in 24 parts of boiling alcohol of sp. gr. 0·798, in 672 parts of water at 10·5° and in 576 parts at 25°,[3] being more readily soluble in alkalis. The aqueous solution shows a blue fluorescence, which is rendered more prominent by the addition of alkalis. A very dilute solution, for example, only showing a faint shimmer, acquires a splendid sky-blue fluorescence when spring water is added to it. One part of æsculin can thus be detected in 15,000,000 parts of water (Trommsdorff). Acids destroy the fluorescence, but it reappears on neutralization. Æsculin dissolves in a small quantity of nitric acid with a yellow colour, which is changed to blood-red by ammonia; 0·2 mgrm. can thus be detected (Sonnenschein).

[1] Zwenger, *ibid.* xc. 65.
[2] Schiff, *Ber. Deutsch. Chem. Ges.* xiv. 303.
[3] *Ann. Chem. Pharm.* xiv. 189.

PHENYLPROPIOLIC GROUP.

2416 *Phenylpropiolic acid,* $C_6H_5.C{\equiv}C.CO_2H$, has been prepared by Glaser by the combination of carbon dioxide with sodium phenylacetylene, the action of sodium and carbon dioxide on β-phenylbromethylene (p. 33) and by heating α-bromocinnamic acid with alcoholic potash,[1] and it is formed in a similar manner from β-bromocinnamic acid.[2] It is readily soluble in alcohol and ether, only slightly in water, from which it crystallizes in long needles, which melt at 137° and are only slightly volatile with steam, melting under water at 80°. When it is distilled with baryta or heated to 120° with water, it decomposes into phenylacetylene and carbon dioxide. Sodium amalgam and water convert it into phenylpropionic acid without the production of cinnamic acid [3] and it combines with bromine to form phenyltetrabromopropionic acid, $C_6H_5.CBr_2.CBr_2.CO_2H$, a substance which has not yet been investigated.

Barium phenylpropiolate crystallizes with various amounts of water, according to the temperature at which it is deposited. If the solution be allowed to evaporate at a low temperature over sulphuric acid, broad plates of $(C_9H_5O_2)_2Ba + 3H_2O$ separate out; at the ordinary temperature, fascicular groups of broad needles, containing two molecules of water, are obtained, while quadratic tablets of $2(C_9H_5O_2)_2Ba + H_2O$ are formed when a hot, saturated solution is allowed to cool slowly. Finally, if this salt be boiled with alcohol, fine needles of the anhydrous salt are obtained.

Copper phenylpropiolate, $(C_9H_5O_2)_2Cu + 4H_2O$, crystallizes from hot water in blue, rhombic plates, which become a green at 80°—90°, with loss of water, carbon dioxide being simul-

[1] *Ann. Chem. Pharm.* cliv. 140.
[2] Barisch, *Journ. Prakt. Chem.* [2], xx. 180.
[3] Erlenmeyer, *Ber. Deutsch. Chem. Ges.* xvi. 152.

taneously evolved and phenylacetylene, which may be recognized by its smell, formed.

Orthonitrophenylpropiolic acid, $C_6H_4(NO_2)C_2.CO_2H$, is readily formed when orthonitrophenyldibromopropionic acid is dissolved in an excess of caustic soda and the solution allowed to stand for some time.[1]

On the addition of hydrochloric acid it separates out in brilliant plates, which crystallize from hot water in almost colourless needles, which decompose suddenly at 155°—156°, leaving a voluminous residue. Its alkali salts crystallize badly; the silver salt is a white precipitate, which explodes very violently on heating.

The acid decomposes on boiling with water into orthonitrophenylacetylene and carbon dioxide, while isatin (p. 73) is formed when it is boiled with alkalis. If its alkaline solution be heated with a little grape-sugar or some other reducing agent, pure indigo-blue separates out, the yield of which amounts to 40 per cent. of the acid employed, while 68 per cent. are required by theory; the loss is mainly due to the formation of isatin (Baeyer).[2]

This reaction is employed to fix indigo in calico-printing; potassium xanthate, which was found by H. Caro to be the best reducing agent for the purpose, is printed on the cloth together with caustic soda and the acid, the material being then dried and steamed.

Ethyl orthonitrophenylpropiolate, $C_6H_4(NO_2)C_2.CO_2.C_2H_5$, crystallizes from ether in large tablets, melting at 60°—61°.

Paranitrophenylpropiolic acid has been prepared by paranitrophenyldibromopropionic acid, which is formed by the combination of bromine with paranitrocinnamic acid.[3] This substance, however, always yields some of the original paranitrocinnamic acid in addition to the nitrophenylpropiolic acid on treatment with alkalis, the bromine being simply eliminated, and it is therefore better to combine ethyl paranitrocinnamate with bromine and treat the ether in hot alcoholic solution with caustic potash.[4]

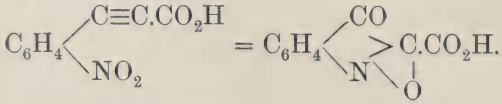
Paranitrophenylpropiolic acid forms a silky, yellow mass or yellow needles, which melt at 198° with evolution of gas and decompose into paranitro-acetylene and carbon dioxide when heated to 140° with water.

[1] Baeyer, *Ber. Deutsch. Chem. Ges* xiii. 2279.
[2] See also Müller, *Ann. Chem. Pharm.* ccxii. 143.
[3] Drewsen, *ibid.* ccxii. 150.
[4] Müller, *ibid.* ccxii. 138; Perkin, *Journ. Chem. Soc.* 1886, i. 440.

Ethyl paranitrophenylpropiolate, $C_6H_4(NO_2)C_2.CO_2.C_2H_5$, crystallizes in long, flat needles, melting at 126°.

Orthamidophenylpropiolic acid, $C_6H_4(NH_2)C_2.CO_2H$, is obtained by the addition of ferrous sulphate solution to a solution of orthonitrophenylpropiolic acid in an excess of ammonia. It forms yellowish, microscopic needles, which are insoluble inwater and decompose on boiling with water, orthamido-acetophenone being formed.[1]

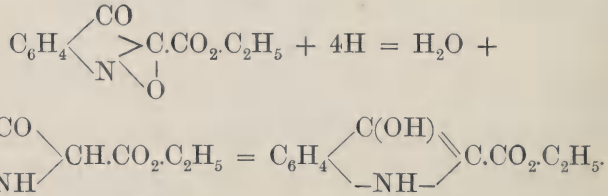
Isatogenic acid, $C_9H_5NO_4$, is formed, as already mentioned (p. 76), when orthonitrophenylpropiolic acid is dissolved in sulphuric acid:



When the solution is poured into water, the isatogenic acid decomposes instantaneously into carbon dioxide and isatin. If, however, ferrous sulphate be added to the sulphuric acid solution, indoïn, $C_{32}H_{20}N_4O_5$, a blue colouring matter, which will be described along with indigo, is formed.

Ethyl isatogenate, $C_9H_4(C_2H_5)NO_4$, is formed by the action of sulphuric acid on ethyl orthonitrophenylpropiolate and crystallizes in yellow needles, melting at 115°.[2]

2417 *Indoxylic acid*, $C_9H_7NO_3$. The ethyl ether of this acid is formed by the action of ammonium sulphide on ethyl orthonitrophenylpropiolate or of zinc and hydrochloric acid on ethyl isatogenate, the ether of the pseudo-acid being the first product and changing into that of indoxylic acid, just as pseudo-isatin changes into isatin:



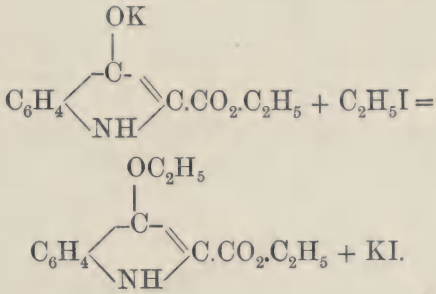
In order to prepare the acid, the ether is brought into caustic soda, which has been treated with a little water and heated to 180° and the product decomposed with dilute sulphuric acid, the

[1] Baeyer and Bloem, *Ber. Deutsch. Chem. Ges.* xv. 2147.
[2] Baeyer, *ibid.* xiv. 1741 ; xv. 780.

indoxylic acid being thus precipitated as a crystalline powder, which melts at 122°—123° with copious evolution of gas.[1] Its dilute alkaline solution rapidly absorbs oxygen with formation of indigo-blue, which is also formed by the action of acid oxidizing agents on the acid, as, for example, when its alkaline solution is heated with orthonitrophenylpropiolic acid.

Ethyl indoxylate forms thick, colourless prisms, melting at 120°—121°, and dissolves in alkalis without decomposition, forming a solution from which it is reprecipitated by carbon dioxide. On heating with sulphuric acid it is converted quantitatively into indigosulphonic acid. When it is boiled with water, indoxyl is formed, which combines with isatin in a hot solution to form indigorubin, an isomeride of indigo.

Ethylindoxylic acid, $C_8H_5(OC_2H_5)NCO_2H$. The ethyl ether of this body is the product of the action of ethyl iodide and caustic potash on ethyl indoxylate, which therefore behaves as a phenol:

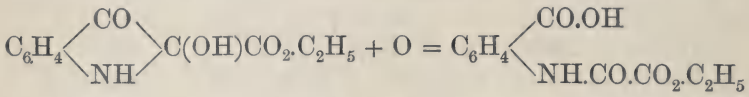


It forms large, colourless crystals, melting at 98°. In order to prepare the acid, the alcoholic solution of the ether is boiled with baryta and then acidified. It crystallizes in small plates, which melt at 160°. It does not oxidize to indigo in alkaline solution, but the oxidation may be brought about by ferric chloride and hydrochloric acid. Nitrous acid converts it into *ethylnitroso-indoxylic acid*, $C_8H_4(OC_2H_5)N(NO)CO_2H$, which crystallizes from alcohol in large, flat, golden-yellow needles.

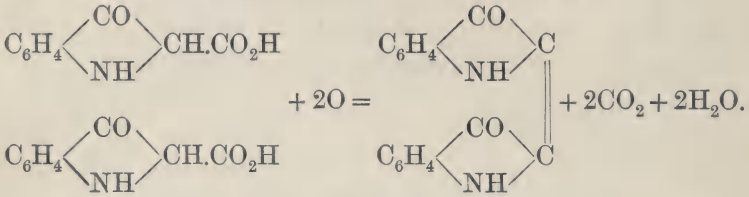
Indoxanthic acid, $C_9H_7NO_4$. The ethyl ether is formed when ethyl indoxylate is carefully oxidized with ferric chloride and crystallizes from ether in straw-yellow needles or long, monosymmetric prisms, which reflect the green and yellow rays and form a deep yellow-coloured solution in water. If this solution be treated with sodium nitrite and then sulphuric acid, *ethyl*

[1] Baeyer, *Ber. Deutsch. Chem. Ges.* xiv. 1742 ; Forrer, *ibid.* xvii. 975.

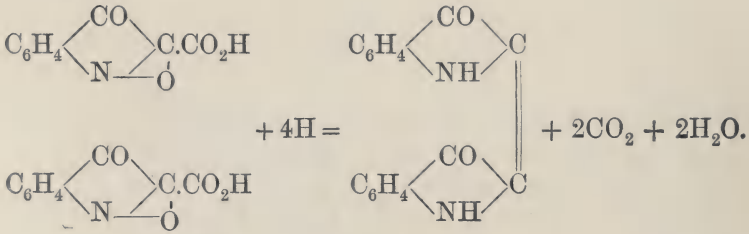
nitroso-indoxanthate, $C_{11}H_{10}(NO)NO_4$, is formed; it crystallizes in yellowish needles or tablets and gives Liebermann's reaction. Indoxylic acid and the ethers of indoxanthic acid are oxidized to ethyloxalanthranilic acid by chromic acid solution, while this yields the original acid on reduction. Ethyl indoxanthate has, therefore, probably the following constitution, which explains the formation of ethyl oxalanthranilic acid in a simple manner:[1]



The formation of indigo-blue from indoxylic acid can be readily explained by assuming that pseudo-indoxylic acid is first formed and then loses carbon dioxide and hydrogen:



In the conversion of orthonitrophenylpropiolic acid into indigo, isatogenic acid is probably the first product and then undergoes reduction:



SUBSTITUTED INDOLS, C_9H_9N.

2418 *Skatol*, C_9H_9N, was discovered by Brieger in human excrements (τὸ σκατὸς, *Fæces*), accompanied by a little indol, but is not present in those of the dog, either during a flesh or a bread diet.[2] Tappeiner found it in the paunch of the cow, while indol alone occurs in both the large and small intestine. In the

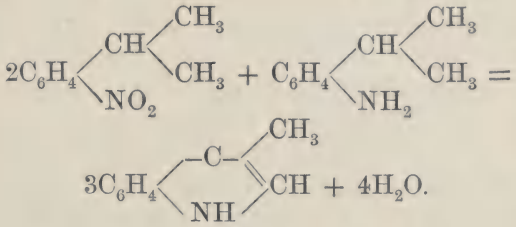
[1] Baeyer, *Ber. Deutsch. Chem. Ges.* xv. 775. [2] *Ibid.* x. 1027.

horse, on the other hand, the latter occurs in the small intestine, phenol alone in the large intestine, and skatol in the colon.[1] The latter is formed, together with indol, by the putrefaction of egg albumen and when this is fused with caustic potash.[2] It is also a product of the putrefaction of flesh,[3] especially in the presence of the pancreatic secretion,[4] and is formed in still greater abundance from the brain of the ox.[5]

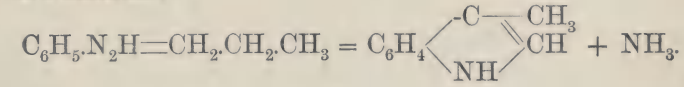
Baeyer found that it may also be obtained, together with indol, from indigo, by reducing this to the yellow compound, which has already been mentioned, and heating this product with zinc dust.[6] O. Fischer and German prepared it by heating aniline zinc chloride with glycerol :[7]

$$C_6H_7N + C_3H_8O_3 = C_9H_9N + 3H_2O.$$

Fileti prepared it from orthonitrocumic acid, $C_6H_3(NO_2)CH(CH_3)_2CO_2H$, by distilling the barium salt with iron filings or zinc dust, but obtained a better yield by heating a mixture of this salt with orthamidocumic acid and caustic baryta.[8] A mixture of orthonitrocumene and orthamidocumene is formed and undergoes the following decomposition :



Its constitution has been decisively determined by E. Fischer. When propidenephenylhydrazone, an oily liquid, which is formed by the action of phenylhydrazine on propionaldehyde, is mixed with an equal weight of powdered zinc chloride, a vigorous reaction ensues, the mixture being finally heated to 180° for one or two minutes :



[1] *Ber. Deutsch. Chem. Ges.* xiv. 2382.
[2] Nencki, *Journ. Prakt. Chem.* [2], xvii. 98.
[3] E. and H. Salkowski, *Ber. Deutsch. Chem. Ges.* xii. 648 ; xviii. 79.
[4] Brieger, *ibid.* xii. 1985.
[5] Nencki, *Hoppe-Seyler's Zeitschr.* iv. 371.
[6] *Ber. Deutsch. Chem. Ges.* xiii. 2339.
[7] *Ibid.* xvi. 710.
[8] *Ibid.* xvi. 2927.

The skatol is purified by distillation with steam.[1] It also occurs among the products of the distillation of strychnine with lime.[2] It crystallizes from hot water or better from petroleum-spirit in dazzling white plates, melts at 95° and boils at 265°—266°. According to Nencki and Brieger it possesses a persistent fæcal odour, while Baeyer describes the odour as simply sharp, and is confirmed by O. Fischer and German, who, however, add that in the finely divided condition, as on the hands and clothes, it has a most unpleasant small. E. Fischer, on the other hand, states that even after being converted into the nitrosamine and again prepared from this it possesses an intense adhering odour of fæces.[3]

A splinter of pine-wood moistened with strong hydrochloric acid is not coloured by an aqueous or alcoholic solution of skatol, while if the splinter be moistened with a hot alcoholic solution and be then brought into cold concentrated hydrochloric acid, it is coloured cherry-red and finally dark violet.

When sodium nitrite is added to a solution of skatol in cold glacial acetic acid, a dark brown colouration is produced and the nitrosamine is precipitated by the addition of water as a yellow oil, which solidifies in a freezing mixture to a crystalline mass. It gives Liebermann's reaction and is reconverted into skatol by zinc dust and dilute acids. Its formation is very characteristic and can be employed for the distinction and separation of skatol from indol and methylketol (E. Fischer).

The picrate is precipitated in red needles when hot aqueous solutions of picric acid and skatol are mixed.

Skatolsulphuric acid, $C_9H_8NSO_4H$, appears as the potassium salt in the urine when skatol is taken internally; it has been observed by J. G. Otto in considerable quantity in a case of diabetes, and obtained from boiling alcohol in crystals.[4]

Hydroskatol, $C_9H_{11}N$, is formed when zinc dust and hydrochloric acid are gradually added to a boiling alcoholic solution of skatol and is an oily liquid, which boils at 231°—232°, smells somewhat like quinoline and piperidine and readily combines with acids. Its platinichloride forms fine needles, only slightly soluble in water and its nitrosamine is an oily liquid.[5]

[1] *Ann. Chem. Pharm.* ccxxxvi. 137.

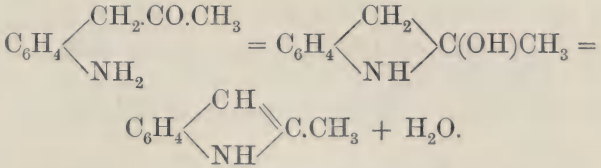
[2] Stoehr, *Ber. Deutsch. Chem. Ges.* xx. 1108.

[3] H. Kopp remarks on the compound ethers: "The odour of these compounds is difficult to define and is often differently described by different investigators (butyric ether smells to some like old cheese, to others like pine-apple)," *Pogg. Ann.* lxxii. 259.

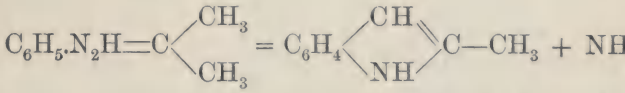
[4] *Ber. Deutsch. Chem. Ges.* xvii. Ref. 380.

[5] Wenzing, *Ann. Chem. Pharm.* ccxxxix. 239.

2419 *Methylketol*, C_9H_9N, is formed by the action of zinc dust and ammonia on orthonitrobenzylmethylketone, this being reduced to amidobenzylmethylketone, which then passes into methylketol with elimination of water, the changes probably taking place as follows:[1]



It is also obtained when acetonephenylhydrazone is heated with five parts of zinc chloride, at first on the water-bath and finally to 180° in an oil bath:[2]



Methylketol crystallizes from hot water in needles and from alcohol in plates, which melt at 60° and have a similar smell to indol. It melts at 272° and its vapour has a sp. gr. of 4·75;[3] it colours a pine splinter moistened with hydrochloric acid red, similarly to indol; nitrous acid produces a yellow colouration in its aqueous solution, followed by an amorphous, yellow precipitate, while, when sodium nitrite is added to a solution in glacial acetic acid, a dark red colouration is produced and water then produces a reddish brown precipitate, which does not give Liebermann's reaction. It differs from indol and skatol in forming a platinichloride, $(C_9H_9N.HCl)_2PtCl_4$, which crystallizes in yellow needles. Its picrate crystallizes in fine, yellowish-red needles. Methylketol is oxidized by potassium permanganate to acetorthamidobenzoic acid (Pt. IV. p. 239), which is therefore formed in an analogous manner to oxalorthamidobenzoic acid from carbostyril (p. 223).

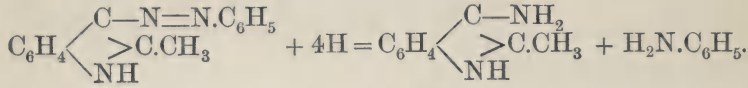
Amidomethylketol. When crystallized sodium acetate and then an alcoholic solution of methylketol are added to a solution of diazobenzene chloride, *methylketolazobenzene* is formed; it separates from hot petroleum-spirit in small, compact, red crystals

[1] Baeyer and Jackson, *Ber. Deutsch. Chem. Ges.* xiii. 187; Jackson, *ibid.* xiv. 879.

[2] Fischer, *Ann. Chem. Pharm.* ccxxxvi. 126.

[3] Treadwell, *Ber. Deutsch. Chem. Ges.* xiv. 1466.

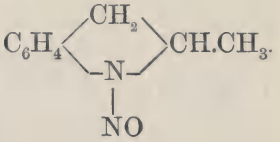
and melts at 115°—116°. It is converted into amidomethylketol by the action of hydrochloric acid and tin :

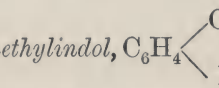


This crystallizes in small plates, which melt at 112°—113° and rapidly become coloured pink and finally dark red in the air. The hydrochloride forms well-developed prisms. On heating with zinc dust and hydrochloric acid the following compound is obtained.[1]

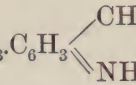
Hydromethylketol, $C_9H_{11}N$, may also be prepared by heating methylketol with tin and hydrochloric acid and is a colourless, oily liquid, which has a characteristic pungent odour, resembling that of piperidine, and boils at 227°—228° (Wenzing). It is a strong base and forms a platinichloride, which crystallizes in octohedra. Acetic anhydride acts upon it with formation of *acetylhydromethylketol*, $C_9H_{10}NCO.CH_3$, which crystallizes from petroleum-spirit in concentrically grouped needles, which melt at 55°—56°.

Nitrosohydromethylketol, $C_9H_{10}N.NO$, is formed when sodium nitrite is added to a solution of hydromethylketol in hydrochloric acid (Jackson) and separates from petroleum-spirit in compact yellow crystals, which melt at 54°—55°. It is reconverted into hydromethylketol by the action of tin and hydrochloric acid and gives Liebermann's reaction, so that it probably possesses the following constitution :



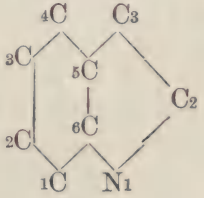
2420 *Dimethylindol*,  , is obtained by heating acetonemethylphenylhydrazone, $C_6H_5.N_2(CH_3)=C(CH_3)_2$, with zinc chloride to 130° and crystallizes from hot petroleum-spirit in fine needles, which melt at 56°, volatilize without decomposition and are slightly soluble in water, readily in alcohol and concentrated hydrochloric acid. This last solution colours a pine splinter in the same way as indol. Dimethylindol picrate crystallizes from benzene in fine, dark red needles.[2]

[1] Wagner, *Ann. Chem. Pharm.* ccxlii. 383. [2] Degen, *ibid.* ccxxxvi. 153.

B3-Methylindol, $CH_3.C_6H_3$  , is prepared by heating B3-Pr2-methylindolcarboxylic acid, a substance which will be subsequently described. It crystallizes from hot water in colourless needles, which melt at 58·5° and cannot be distinguished from indol by the smell or other general properties.[1]

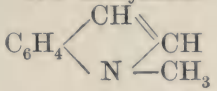
In addition to these bodies, other substituted indols are also known, some which will be subsequently described. They are designated by the following nomenclature, which has been proposed by E. Fischer:

"The nitrogenous ring of indol, which is actually a pyrrol ring, receives the symbol Pr and the numbering of the component atoms commences in the pyrrol ring at the nitrogen and in the benzene ring at the corresponding carbon atom, as shown in the following diagram:"

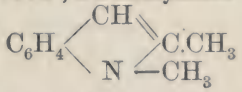


In order to avoid errors, an *n* is added as an index to the number representing the position of the nitrogen atom, when necessary; thus we have the following names:[2]

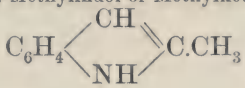
Pr 1^n-Methylindol.



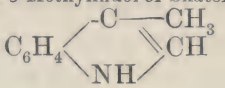
Pr 1^n, 2-Dimethylindol.



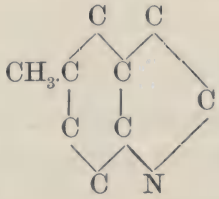
Pr 2-Methylindol or Methylketol.



Pr 3-Methylindol or Skatol.



If substitution take place in the aromatic nucleus, the symbol B is prefixed to the number. The formula of B3-methylindol is therefore:

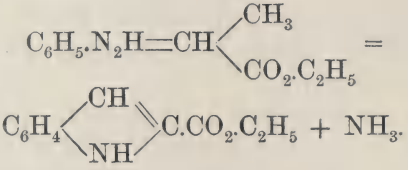


[1] Raschen, *Ann. Chem. Pharm.* ccxxxix. 223.

[2] *Ibid.* ccxxxvi. 121.

INDOLCARBOXYLIC ACID, $C_9H_7NO_2$.

2421 The ethyl ether of this acid is formed when the phenylhydrazone of pyroracemic acid is heated to 195° with zinc chloride:



It crystallizes in white prisms and is readily hydrolysed by heating with a little alcohol and fairly concentrated caustic potash solution. On the addition of dilute sulphuric acid to the solution, the indolcarboxylic acid is precipitated as a crystalline mass; it separates from boiling water in long, fine needles, which melt at 200° to a red liquid and decompose at 230° into carbon dioxide and indol, which, however, for the most part undergoes a further change at this temperature.

It does not give any colouration with a pine splinter moistened with hydrochloric acid. The picrate separates in golden-yellow needles when the acid is brought together with picric acid in ethereal solution. When nitric acid is added to its solution in glacial acetic acid, yellow crystals are precipitated after some time, which form a deep red solution in alkalis.[1]

Methylindolcarboxylic acid, $C_8H_5(NCH_3)CO_2H$, is formed by the action of hydrochloric acid on the methylphenylhydrazone of pyroracemic acid and crystallizes from hot alcohol in white needles, which melt at 212° and gradually decompose into carbon dioxide and methylindol.

Ethylindolcarboxylic acid, $C_8H_5(NC_2H_5)CO_2H$, forms colourless needles, melting at 183°.

Phenylindolcarboxylic acid, $C_8H_5(NC_6H_5)CO_2H$. When pyroracemic acid and diphenylhydrazine are brought together in ethereal solution, the mixture becomes warm and the diphenylhydrazone of pyroracemic acid separates out after a short time in crystals, which readily form a yellow solution in hot benzene, less readily in ether and cold alcohol and crystallize from hot

[1] Fischer, *Ann. Chem. Pharm.* ccxxxvi. 141.

alcohol in white needles, melting at 145°. If it be dissolved in glacial acetic acid, fuming hydrochloric acid added and the mixture heated on the water-bath, phenylindolcarboxylic acid is formed and crystallizes from dilute alcohol in white needles, melting at 176°.[1]

Benzylindolcarboxylic acid, $C_8H_5(NCH_2.C_6H_5)CO_2H$, has been obtained from benzylaniline by reducing the nitrosamine with zinc dust and glacial acetic acid and treating the resulting benzylphenylhydrazine with pyroracemic acid. The oily product thus obtained yields benzylindolcarboxylic acid on heating with hydrochloric acid. It crystallizes from hot glacial acetic acid in compact needles, which melt at 195° with evolution of gas.[2]

[1] Fischer and Hess, *Ber. Deutsch. Chem. Ges.* xvii. 559.
[2] Antrick, *Ann. Chem. Pharm.* ccxxvii. 360.

THE CYMENE GROUP.

2422 The following hydrocarbons of the general formula $C_{10}H_{14}$ are known:

s-Tetramethylbenzene or durene
a-Tetramethylbenzene or isodurene
v-Tetramethylbenzene or prehnitene
} $C_6H_2(CH_3)_4$.

Ethylparaxylene
s-Ethylmetaxylene
a-Ethylmetaxylene
a-Ethylorthoxylene
} $C_6H_3\begin{cases}CH_3\\C_2H_5\\CH_3\end{cases}$

Paradiethylbenzene
Metadiethylbenzene
} $C_6H_4(C_2H_5)_2$.

Paramethylpropylbenzene or cymene
Orthomethylpropylbenzene or orthocymene
Metamethylpropylbenzene or metacymene
} $C_6H_4\begin{cases}CH_3\\C_3H_7\end{cases}$.

Para-isocymene
Meta-isocymene
} $C_6H_4<\begin{matrix}CH_3\\CH(CH_3)_2\end{matrix}$

Butylbenzene, $C_6H_5.C_4H_9$.
a-Isobutylbenzene, $C_6H_5.CH_2.CH(CH_3)_2$.
β-Isobutylbenzene, $C_6H_5.CH<\begin{matrix}CH_3\\C_2H_5\end{matrix}$.

Cymene, which occurs in nature, is the member of this group with which chemists have been acquainted for the longest time. The others have been artificially prepared and some of them have also been found in rock-oil and in the products of the dry distillation of resin and coal.

THE TETRAMETHYLBENZENES, $C_6H_2(CH_3)_4$.

s-Tetramethylbenzene (1 : 2 : 4 : 5) was first prepared by Fittig and Jannasch by the action of sodium on a mixture of methyl iodide and bromopseudocumene and named *durene*, because it differs from the benzenehydrocarbons, which were then known, in being solid (*durus*) at the ordinary temperature.[1] A better yield is obtained by employing dibromometaxylene[2] or dibromoparaxylene.[3] It is also formed by the action of methyl chloride on a mixture of toluene and aluminium chloride,[4] orthoxylene, accompanied by small quantities of its two isomerides, being the first product. This yields pseudocumene almost exclusively on further methylation and the latter is then converted into durene, which can therefore be readily prepared by passing methyl chloride, dried by sulphuric acid, into a mixture of one part of aluminium chloride and five parts of pseudocumene at a temperature of 75°—85°.[5]

Durene is also formed in small amount, when oil of turpentine is passed through a red-hot tube[6] and occurs in Baku petroleum[7] and coal-tar.[8]

It is readily soluble in alcohol, ether and benzene, and crystallizes from the last two in large tablets or prisms, while it separates from petroleum-spirit in clear, strongly refractive monosymmetric crystals. It possesses an odour resembling that of camphor, melts at 80°, boils at 191°—192° and gradually sublimes even at the ordinary temperature in plates or tablets. On heating with phosphorus pentachloride, the chloride $C_6H_2(CH_2Cl)_4$ is formed, which separates from ether in crystals, melting at 144°, which are converted into the alcohol, $C_6H_2(CH_2.OH)_4$, by continued heating with very dilute caustic potash solution; the latter forms a bitter, elastic mass, only slightly soluble in water.[9]

[1] *Zeitschr. Chem.* 1870, 161.
[2] Jannasch, *Ber. Deutsch. Chem. Ges.* vii. 692; Gissmann, *Ann. Chem. Pharm.* ccxvi. 200.
[3] Jannasch, *Ber. Deutsch. Chem. Ges.* x. 1354.
[4] Friedel and Crafts, *Ann. Chim. Phys.* [6], i. 449; Ador and Rilliet, *Ber. Deutsch. Chem. Ges.* xii. 329.
[5] Jacobsen, *ibid.* xiv. 2624.
[6] Montgolfier, *Ann. Chim. Phys.* [5], xix. 164.
[7] Markownikow, *Ann. Chem. Pharm.* ccxxxiv. 114.
[8] Schulze, *Ber. Deutsch. Chem. Ges.* xviii. 30.
[9] Colson, *Bull. Soc. Chim.* xlvi. 198.

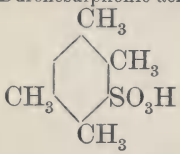
Bromodurene, $C_6HBr(CH_3)_4$, crystallizes from hot alcohol in nacreous plates, melting at 61°.

Dibromodurene, $C_6Br_2(CH_3)_4$, forms long, thin needles, melting at 199°, which are scarcely soluble in cold alcohol.

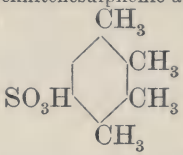
Dinitrodurene, $C_6(NO_2)_2(CH_3)_4$, crystallizes in rhombic prisms and melts at 205°.

Durenesulphonic acid, $C_6H(SO_3H)(CH_3)_4$, is only formed with difficulty when durene is allowed to stand in contact with sulphuric acid for six to eight hours, the mixture being frequently stirred, while durene is liberated if the previously prepared sulphonic acid or its anhydrous sodium salt is treated with sulphuric acid. If, however, the mixture be allowed to stand for some days and be then heated for some hours to 40°—50°, a small quantity of hexmethylbenzene, $C_6(CH_3)_6$, is formed, together with the sulphonic acid of v-tetramethylbenzene or prehnitene and β- and γ-pseudocumenesulphonic acids, which are also obtained by heating durene with sulphuric acid:

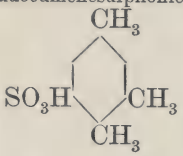
Durenesulphonic acid.



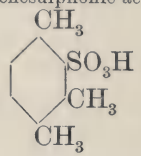
Prehnitenesulphonic acid.



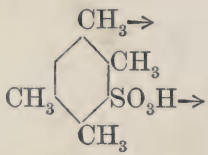
β-Pseudocumenesulphonic acid.

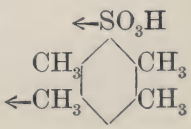


γ-Pseudocumenesulphonic acid.



The last two cannot be formed directly from pseudocumene, since the α-compound would in this case be the product, and they are therefore probably formed by the elimination of two different methyl groups from durenesulphonic acid. In the conversion of durenesulphonic acid into prehnitenesulphonic acid, a change of position of two of the side chains takes place, perhaps in the following way:[1]





[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* xix. 1209.

It may however also be formed by the combination of methyl with β-pseudocumenesulphonic acid.

Durenesulphonic chloride, $C_6H(SO_2Cl)(CH_3)_4$, is formed, together with the sulphonic acid, when durene is brought into ice-cold chorosulphonic acid, $SO_2(OH)Cl$, and crystallizes from ether in brittle, vitreous prisms, which melt at 99°.

Durenesulphamide, $C_6H(SO_2.NH_2)(CH_3)_4$, separates from alcoholic solution in long prisms, melting at 155°.

Durenol, $C_6H(OH)(CH_3)_4$, is obtained by fusing the sulphonic acid with caustic potash, and crystallizes from hot alcohol in large, flat prisms, melting at 117°. It boils at 249° and sublimes very readily at its melting-point.[1]

Duroquinone, $C_6(CH_3)_4O_2$. Dinitrodurene is reduced by the action of zinc dust on its acetic acid solution to diamidodurene, which crystallizes in lustrous tablets and is oxidized by ferric chloride to the quinone; this crystallizes from petroleum-spirit in long, yellow needles, which melt at 111°, readily sublime and have a smell resembling that of quinone. It is readily reduced by sulphurous acid, &c., but the quinol, which is thus formed, rapidly re-oxidizes in the air.[2]

2423 *α-Tetramethylbenzene* or *Isodurene* (1 : 3 : 4 : 5) was obtained by Jannasch by the action of sodium on a mixture of bromomesitylene and methyl iodide.[3] It is also formed, together with pentamethylbenzene and hexmethylbenzene, when methyl chloride is passed into a heated mixture of mesitylene and aluminium chloride,[4] and by the action of concentrated sulphuric acid on pentamethylbenzene.[5] Armstrong and Miller have also obtained it, accompanied by metacymene, by the action of zinc chloride or iodine on camphor;[6] Markownikow detected its presence in petroleum from Baku, and Schulze in coal-tar.[7] It is a liquid, which possesses a faint aromatic odour, boils at 195°[8] and does not solidify in a freezing mixture.

Bromisodurene, $C_6HBr(CH_3)_4$, is a liquid, which boils at 252°—254° and solidifies at a very low temperature to plates, which have a fine nacreous lustre.[9]

Dibromisodurene, $C_6Br_2(CH_3)_4$, forms needles melting at 209°.

[1] Jacobsen and Schnapauff, *Ber. Deutsch. Chem. Ges.* xviii. 284.
[2] Nef, *ibid.* xviii. 2806; *Ann. Chem. Pharm.* ccxxxvii. 4.
[3] *Ber. Deutsch. Chem. Ges.* viii. 355.
[4] Jacobsen, *ibid.* xiv. 2629.
[5] *Ibid.* xix. 1216.
[6] *Ibid.* xvi. 2255.
[7] *Ibid.* xx. 409.
[8] *Ibid.* xv. 1853.
[9] Bielefeldt, *Ann. Chem. Pharm.* cxcviii. 380.

Dinitro-isodurene, $C_6(NO_2)_2(CH_3)_4$, crystallizes from hot alcohol in fine, transparent prisms and melts at 156°.

If metaxylene be heated with aluminium chloride, the operation being most advantageously conducted in a current of hydrochloric acid, isodurene, durene, pseudocumene, mesitylene, paraxylene, toluene and benzene are formed. The same products are obtained from pseudocumene and mesitylene, and other aromatic hydrocarbons behave in a similar manner, a simultaneous analysis and synthesis being effected.

Isomeric hydrocarbons are in this way apparently converted into one another, as, for example, metaxylene into paraxylene, the latter being however actually formed from toluene, which is also present among the products. Another instance is the apparent conversion of pseudocumene into mesitylene and *vice versâ*.[1]

Isodurenol, $C_6H(OH)(CH_3)_4$, has been prepared from isoduridine and forms white crystals, melting at 80°—81°.

Isoduridine, $C_6H(NH_2)(CH_3)_4$, occurs among the by-products of the preparation of *a*-pseudocumidine,[2] and is also formed when the hydrochloride of the latter, or that of mesidine, is heated to 300° with methyl alcohol.[3] It is an oily liquid, which boils at 250°—253°, and solidifies on cooling to crystals, which melt at 14°.

Tetramethylphenylcarbamine, $C_6H(NC)(CH_3)_4$, is formed by the action of chloroform and alcoholic potash on the preceding compound. It possesses the characteristic smell of the carbamines, melts at 51° and is converted into the nitril by heating to 240°. The latter melts at 68°—69° and is only attacked by hydrochloric acid at 250°, at which temperature the corresponding acid is not formed, its decomposition products, carbon dioxide and isodurene, being obtained.

2425 *v-Tetramethylbenzene* or *Prehnitene* (1 : 2 : 3 : 4) was obtained by Jacobsen, who converted durene into prehnitenesulphonic acid as already described, and separated this from the accompanying pseudocumenesulphonic acid by converting the mixture into the amides and recrystallizing these from alcohol. Pure prehnitene was obtained by heating the corresponding sulphamide, which is the less soluble and melts at 18·7°, with

[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* xviii. 338 ; Anschütz and Immendorff, *ibid.* xviii. 657 ; Anschütz, *Ann. Chem. Pharm.* ccxxxv. 150.
[2] Hofmann, *Ber. Deutsch. Chem. Ges.* xvii. 1912.
[3] Nölting and Baumann, *ibid.* xviii. 1147.

hydrochloric acid to 170°—180°. It is a liquid, which boils at 204° and solidifies at a low temperature to a macrocrystalline mass, melting at −4°.

Prehnitenesulphonic acid, accompanied by hexmethylbenzene, was subsequently obtained by Jacobsen as the product of the action of sulphuric acid upon pentamethylbenzene, $C_6H(CH_3)_5$, and this renders it probable that in the conversion of durene into prehnitene, the former passes first into pseudocumene and pentamethylbenzene.[1]

Dibromoprehnitene, $C_6Br_2(CH_3)_4$, crystallizes from a mixture of toluene and alcohol in long prisms, melting at 210°.

Dinitroprehnitene, $C_6(NO_2)_2(CH_3)_4$, separates from alcohol in compact, vitreous prisms, melting at 178°.[2]

Friedel and Crafts, and Ador and Rilliet, have obtained a tetramethylbenzene by the action of methyl chloride on toluene in the presence of aluminium chloride, which boils at 185°—190° and probably consists chiefly of isodurene, while Kelbe and Pathe have obtained a substance by heating *v*-bromopseudocumene with methyl iodide and sodium, which distils at 170°—190°[3] and must, according to its formation, be impure prehnitene.

TRIMETHYLBENZENECARBOXYLIC ACIDS, $C_6H_2(CH_3)_3CO_2H$.

The position of the carboxyl group in the following compounds is designated by the number 1.

2426 *Duric acid* (1 : 2 : 4 : 5) was obtained by Jannasch, who named it *cumic acid*, by the oxidation of durene with nitric acid.[4] A solution of chromium trioxide in glacial acetic acid may also be employed as the oxidizing agent.[5] Reuter prepared it by fusing potassium *a*-pseudocumenesulphonate with sodium formate.[6] It is, however, best prepared by acting upon diazopseudocumene chloride with a solution of copper sulphate and potassium cyanide, *duronitril*, $C_6H_2(CH_3)_3CN$, which crystallizes from alcohol in long needles, melts at 57·5° and boils at

[1] *Ber. Deutsch. Chem. Ges.* xx. 900.
[2] *Ibid.* xix. 1209.
[3] *Ibid.* xix. 1551.
[4] *Zeitschr. Chem.* 1870, 449; Nef, *Ber. Deutsch. Chem. Ges.* xviii. 2801.
[5] Gissmann, *Ann. Chem. Pharm.* ccxvi. 205.
[6] *Ber. Deutsch. Chem. Ges.* xi. 29.

250°, being formed. This is converted into the acid by continued boiling with alcoholic potash.[1] The latter is scarcely soluble in water, volatilizes with steam and crystallizes from hot benzene in needles, frequently an inch in length and having a splendid lustre, while it separates from alcohol in prisms, melting at 149°—150°.

Dinitroduric acid, $C_6(NO_2)_2(CH_3)_3CO_2H$, is best prepared by adding well-cooled solutions of potassium nitrate and duric acid to sulphuric acid. It forms a yellow powder, which is only slightly soluble in cold, more readily in hot water and melts at 205°. It crystallizes from dilute alcohol or alcoholic ether in prisms containing alcohol of crystallization, which is readily given off, the acid being left as an amorphous powder.[2]

Diamidoduric acid, $C(NH_2)_2(CH_3)_3CO_2H$, is formed by the action of zinc dust and dilute acetic acid on the preceding compound. It crystallizes from hot water in silky, matted needles, which melt at 221° with decomposition.[3]

Hydroxyduric acid, $C_6H(OH)(CH_3)_3CO_2H$, is obtained when durenol is fused for a considerable time with caustic potash and crystallizes from dilute alcohol in small needles, melting at 148°, which readily sublime. Its alcoholic solution gives a fugitive blue colouration with ferric chloride, which produces a dirty brown precipitate in solutions of its salts. On heating to 200° with hydrochloric acid, β-pseudocumenol is formed.[4]

Pseudocumoquinonecarboxylic acid, $C(CH_3)_3O_2(CO_2H)$, was obtained by Nef by the oxidation of a solution of diamidoduric acid in hydrochloric acid with ferric chloride. It separates from an ethereal solution as an oily liquid, which after some hours changes into deep golden-yellow, feathery groups of needles which have a distinct quinone-like odour and decompose at 130° with evolution of gas.

Dihydroxyduric acid or *Pseudocumoquinolic acid*, $C(CH_3)_3(OH)_2CO_2H$, is formed by the reduction of the quinone-acid in alkaline solution with zinc dust, and crystallizes from hot water in spherical aggregates of needles, which melt with decomposition at 210° and form a deep violet coloured solution in alkalis. Ferric chloride re-oxidizes it in acid solution with production of

[1] Haller, *Ber. Deutsch. Chem. Ges.* xviii. 93; Nef, *Ann. Chem. Pharm.* ccxxxvii. 3.
[2] Gissmann, *loc. cit.*; Nef, *loc. cit.*
[3] Nef, *Ber. Deutsch. Chem. Ges.* xviii. 3496.
[4] Jacobsen and Schnapauff, *ibid.* xviii. 2841.

a green colouration to the quinone-acid, which forms the first instance of a benzoquinonecarboxylic acid.[1]

2427 *a-Isoduric acid* (1 : 3 : 4 : 5) was first obtained by Bielefeldt by the oxidation of isodurene,[2] and it was then shown by Jacobsen that the other isoduric acids which are theoretically possible are simultaneously formed by this method.[3] The mixture of acids is converted into the barium salts, that of *a*-isoduric acid being readily deposited in crystals. The acid, which is liberated from this, is only slightly soluble in water, and separates from alcohol, in which it readily dissolves, in compact prisms, and from ether in large, transparent, strongly refractive, monosymmetric crystals. It melts at 215°, readily sublimes in long, lustrous needles, is volatile with steam and yields hemellithene on distillation with lime.

β-Isoduric acid (1 : 2 : 4 : 6) is separated from the γ-acid by repeated recrystallization from petroleum-spirit, in which the latter is more readily soluble. It separates on evaporation in hard, lustrous, transparent prisms, which melt at 151° and yield pure mesitylene on distillation with lime.

γ-Isoduric acid (1 : 2 : 3 : 5) crystallizes from dilute alcohol in needles, which melt at 84°—85° and readily volatilize with steam. It is scarcely soluble in cold, readily in hot water, and on distillation with lime yields pseudocumene.

Prehnitic acid (1 : 2 : 3 : 4) is formed, unaccompanied by any isomeride, by boiling prehnitene with dilute nitric acid. It crystallizes from hot alcohol in long, transparent, vitreous prisms, which melt at 167·5° and volatilize tolerably readily with steam. On distillation with lime, it decomposes into carbon dioxide and hemellithene.[4]

DIMETHYLBENZENEDICARBOXYLIC ACIDS, $C_6H_2(CH_3)_2(CO_2H)_2$.

2428 *a-Cumidic acid* (1 : 3 : 4 : 6). Jannasch, by the oxidation of durene, obtained duric acid and also the dibasic cumidic acid,[5] which, however, was shown by Schnapauff to be a mixture of two isomerides, which are also formed by the

[1] Nef, *Ann. Chem. Pharm.* ccxxxvii. 1.
[2] *Ber. Deutsch. Chem. Ges.* xv. 1853.
[3] *Ibid.* cxcviii. 380.
[4] Jacobsen, *ibid.* xix. 1209.
[5] *Zeitschr. Chem.* 1871, 33.

oxidation of duric acid with potassium permanganate and can readily be separated by means of their methyl ethers.

α-Cumidic acid is also formed when dibromometaxylene is heated under pressure with ethyl chlorocarbonate and sodium amalgam. It is only slightly soluble in water, more readily in hot alcohol, from which it crystallizes in microscopic, vitreous prisms, which sublime on heating in fine plates without previously melting. It yields metaxylene on distillation with lime.

Methyl-α-cumidate, $C_6H_2(CH_3)_2(CO_2.CH_3)_2$, crystallizes from wood-spirit in long needles, resembling asbestos, or large, thin tablets, melting at 76°.

β-Cumidic acid (1 : 4 : 2 : 5) crystallizes from alcohol in six-sided prisms, which sublime in small plates and decompose into carbon dioxide and paraxylene on distillation with lime.

Methyl β-cumidate is less soluble in methyl alcohol than the *α*-compound and crystallizes in long, flat needles, which have a diamond lustre and melt at 114°.[1]

Isocumidic acid (1 : 3 : 5 : 6) was obtained by Jacobsen by the oxidation of a mixture of *β*- and *γ*-isoduric acid. It melts at 278°—280° and sublimes at a slightly higher temperature in small, transparent crystals. On heating with lime, it yields metaxylene.[2]

BENZENETETRACARBOXYLIC ACIDS, $C_6H_2(CO_2H)_4$.

2429 *Pyromellitic acid* (1 : 2 : 4 : 5) was prepared by Erdmann by the distillation of mellitic acid, $C_6(CO_2H)_6$, and by heating its salts with sulphuric acid,[3] and was then investigated by Baeyer.[4] It is also formed by the oxidation of duric or cumidic acid with potassium permanganate (Jacobsen).[5]

It is best prepared by slowly distilling a mixture of two parts of sodium mellitate and three parts of sulphuric acid. It crystallizes in asymmetric tablets, containing two molecules of water which are expelled at 110°, and is tolerably soluble in water and readily in alcohol.

[1] *Ber. Deutsch. Chem. Ges.* xix. 2506.
[2] *Ibid.* xv. 1853.
[3] *Ann. Chem. Pharm.* lxxx. 281.
[4] *Ibid.* Suppl. vii. 35, 166, 325.
[5] *Ber. Deutsch. Chem. Ges.* xviii. 2516.

The normal salts alone have hitherto been prepared, and Erdmann on this account considered it as a monobasic acid of the formula C_5HO_4(C = 6, O = 8), adding that it might also be a dibasic acid of the formula $C_{10}H_3O_8$, which was doubled by Gerhardt for reasons which will be given under mellitic acid.

The ethers are obtained by the action of the alcoholic iodides on the silver salt.

Methyl pyromellitate, $C_6H_2(CO_2.CH_3)_4$, crystallizes in large plates, which are only slightly soluble in boiling alcohol and melt at 138°.

Ethyl pyromellitate, $C_6H_2(CO_2.C_2H_5)_4$, forms short, flat needles, melting at 53°, and is, like the methyl ether, volatile without decomposition (Baeyer).

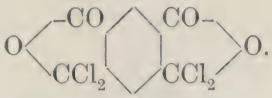
Dinitropyromellitic acid, $C_6(NO_2)_2(CO_2H)_4$, is obtained by the oxidation of dinitroduric acid with potassium permanganate, and crystallizes in long, silky needles, which have a strongly acid taste.[1]

Ethyl dinitropyromellitate, $C_6(NO_2)_2(CO_2.C_2H_5)_4$, is prepared by the action of ethyl iodide on the silver salt; it crystallizes from alcohol in needles, melting at 130°.

Ethyl diamidopyromellitate, $C_6(NH_2)_2(CO_2.C_2H_5)_4$, is formed when the acetic acid solution of the preceding compound is treated with zinc dust, and crystallizes from ether in deep fiery-red, lustrous prisms, which melt at 134° and volatilize without decomposition.

Pyromellitic anhydride, $C_{10}H_2O_6$, sublimes, when the acid is heated, in long needles, melting at 286°, which readily dissolve in water, the acid being reproduced.

Pyromellityl chloride, $C_{10}H_2O_4Cl_4$, is formed when the acid is heated for some time with phosphorus chloride; it is a crystalline mass, which is gradually reconverted into pyromellitic acid by boiling with water. Its constitution is undoubtedly analogous to that of phthalyl chloride:



Hydropyromellitic acid, $C_6H_6(CO_2H)_4$. When pyromellitic acid is treated for some time with water and sodium amalgam, two isomeric compounds are formed, one of which remains behind on evaporation of the ethereal solution as an amorphous

[1] Nef, *Ber. Deutsch. Chem. Ges.* xviii. 2802; *Ann. Chem. Pharm.* ccxxxvii. 19.

mass, while *isohydropyromellitic acid* crystallizes in needles, containing two molecules of water, which become anhydrous at 120° and decompose above 200° with formation of tetrahydrophthalic acid. On heating with sulphuric acid, it yields pyromellitic acid, trimellitic acid and isophthalic acid.

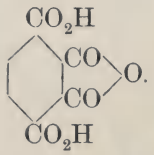
2430 *Mellophanic acid* (1 : 2 : 4 : 6) is formed, together with the isomeric prehnitic and trimesic acids, when hydromellitic acid, $C_6H_6(CO_2H)_6$, is heated with sulphuric acid :

$$(1)\ C_6H_6(CO_2H)_6 + 3SO_4H_2 = C_6H_2(CO_2H)_4 + 2CO_2 + 3SO_2 + 6H_2O.$$

$$(2)\ C_6H_6(CO_2H)_6 + 3SO_4H_2 = C_6H_3(CO_2H)_3 + 3CO_2 + 3SO_2 + 6H_2O.$$

Mellophanic acid is also obtained when isoduric acid is oxidized with potassium permanganate.[1] It is readily soluble in water, forms an indistinct crystalline crust or short prisms and is converted into the anhydride on heating. The latter melts at 238° and solidifies in crystals resembling flowers of ice, which rapidly become indistinct and then melt at 164°. If calcium acetate be added to a solution of the acid, which must not be too dilute, and the solution heated, a flocculent precipitate is formed, which redissolves on cooling (Jacobsen). It is converted by the action of sodium amalgam and water into a hydromellophanic acid, which has not been fully investigated, and yields hemimellitic acid, $C_6H_3(CO_2H)_3$, on heating with sulphuric acid.

Prehnitic acid (1 : 2 : 3 : 4) is also readily soluble in water and crystallizes with two molecules of water in prisms, which resemble the mineral prehnite, lose their water of crystallization at 100° and are converted at a higher temperature into the anhydride, $C_{10}H_4O_7$. This substance melts at 239° and distils as a colourless oil, which solidifies in crystals resembling ammonium chloride. It has probably the following constitution (Jacobsen):



[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* xvii. 2516.

The acid is converted by the action of sodium amalgam and water into *hydroprehnitic acid*, $C_6H_6.(CO_2H)_4$, a gummy mass, which yields isophthalic acid and a little prehnitic acid on heating with sulphuric acid.

Prehnomalic acid, $C_6H_3(OH)(CO_2H)_4$, is formed along with prehnitic acid, &c., especially if the hydromellitic acid be not heated too long with the sulphuric acid. It crystallizes in needles and yields an anhydride, which melts at 210°. On heating with sulphuric acid or by the action of bromine and water, prehnomalic acid is converted into prehnitic acid.[1]

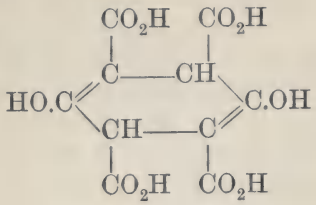
DIHYDROXYBENZENETETRACARBOXYLIC ACIDS, $C_6(OH)_2(CO_2H)_4$.

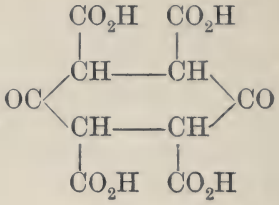
2431 *Dihydroxypyromellitic acid* is obtained by the hydrolysis of its ethyl ether. It crystallizes from hot water in light-yellow prisms or separates on the addition of concentrated hydrochloric acid in broad, flat needles, which contain water. It gives a pure blue colouration with ferric chloride.

Ethyl dihydroxypyromellitate, $C_6(OH)_2(CO_2.C_2H_5)_4$. The product of the action of pure nitric acid on ethyl diamidopyromellitate is *quinonetetracarboxylic ether*, $C_6O_2(CO_2.C_2H_5)_4$, which crystallizes from alcohol in golden-yellow needles, melts at 148°—149° and readily sublimes. It is reduced by zinc dust and glacial acetic acid to the ether of dihydroxypyromellitic acid, which crystallizes in needles, which show a blue reflection, melt at 126°—128° and readily dissolve in alcohol, ether, &c., forming solutions, which have a blue fluorescence. It is converted by the action of zinc dust and hydrochloric acid on its hot alcoholic solution into *ethyl dihydroxydihydropyromellitate* or *ethyl diketohexmethylenetetracarboxylate*, $C_6H_2(OH)_2(CO_2.C_2H_5)_4$. This body crystallizes in splendid, colourless needles, containing water, which is lost at 110°, the compound becoming hard and granular and melting in this state at 142°—144°. It shows the greatest similarity to ethyl succinosuccinate (Pt. IV. p. 517), is reconverted by bromine into the preceding compound, &c.[2]

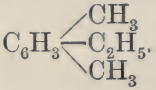
[1] Baeyer, *Ber. Deutsch. Chem. Ges.* iv. 73 ; *Ann. Chem. Pharm.* clxvi. 325.
[2] Nef, *ibid.* ccxxxvii. 19.

The constitution of the corresponding acid is therefore expressed by the following tautomeric formulæ:





THE DIMETHYLETHYLBENZENES,



2432 *Ethylparaxylene* (1 : 2 : 4), was obtained by Jacobsen by the action of sodium on a mixture of bromoparaxylene and ethyl bromide, as a liquid boiling at 185°.[1]

s-Ethylmetaxylene (1 : 3 : 5), is formed when methylethylketone is heated with sulphuric acid,[2] as well as by the action of sodium on a mixture of s-bromometaxylene and ethyl iodide.[3] It is a liquid, which boils at 180° and is converted by oxidation into mesitylenic and uvitic acids.

s-Tribromethylmetaxylene, $C_6Br_3(CH_3)_2C_2H_5$, crystallizes from hot alcohol in long, fine needles, melting at 218°.

s-Trinitro-ethylmetaxylene, $C_6(NO_2)_3(CH_3)_2C_2H_5$, is only slightly soluble in hot alcohol and crystallizes in hard needles, melting at 238° (Jacobsen).

a-Ethylmetaxylene (1 : 4 : 3) has been prepared from a-bromometaxylene and ethyl bromide,[4] and is also formed, together with dixylylethane, $[(CH_3)_2C_6H_3]_2CH.CH_3$, by the action of ethidene chloride on a mixture of metaxylene and aluminium chloride.[5] It is a liquid, which boils at 186°.

a-Tribromethylmetaxylene, $C_6Br_3(CH_3)_2C_2H_5$, crystallizes in small needles and melts at 90°—91° (Anschütz and Romig).

a-Ethylorthoxylene (1 : 4 : 2) occurs among the products of the action of zinc chloride or iodine on camphor; it boils at

[1] *Ber. Deutsch. Chem. Ges.* xix. 2515.
[2] Jacobsen, *ibid.* vii. 1432.
[3] Wroblewsky, *Ann. Chem. Pharm.* cxcii. 217.
[4] Fittig and Ernst, *ibid.* cxxxix. 192.
[5] Anschütz and Romig, *ibid.* ccxxxv. 322.

189°, and is converted by oxidation with dilute nitric acid into paraxylic acid.[1]

The sulphamides of the ethylxylenes, $C_6H_2(SO_2.NH_2)(CH_3)_2C_2H_5$, as deposited from absolute alcohol, are very characteristic compounds (Jacobsen):

	Melting-point.
Ethylparaxylenesulphamide, compact, transparent crystals	117°
a-Ethylmetaxylenesulphamide, vitreous prisms	148°
a-Ethylorthoxylenesulphamide, large, compact prisms	126°

ACIDS, $C_{10}H_{12}O_3$ and $C_{10}H_{10}O_3$.

2433 *Methylethylsalicylic acid*, $C_2H_5.C_6H_2(OH)(CH_3)CO_2H$, was obtained by Jacobsen by fusing the sulphonic acid of s-ethylmetaxylene with caustic potash. It crystallizes from dilute alcohol in long needles, melts at 147°—149° and gives a blue colouration with ferric chloride.[2]

Paraxylylglyoxylic acid, $(CH_3)_2C_6H_3.CO.CO_2H(1:4:2)$. When a mixture of paraxylene and acetyl chloride is acted on by aluminium chloride, *paraxylylmethylketone*, $(CH_3)_2C_6H_3.CO.CH_3$, is formed, as a mobile, strongly refractive liquid, which possesses an aromatic odour, boils at 224°—225° and is oxidized to paraxylylglyoxylic acid by potassium permanganate. Acids separate it from its salts as a thick oil, which solidifies over sulphuric acid to a crystalline mass, melting between 70°—80°, which absorbs water from the air and deliquesces, forming the compound $(CH_3)_2C_6H_3.C(OH)_2CO_2H$. It is oxidized by nitric acid to isoxylic acid and decomposes on distillation into the aldehyde of this and carbon dioxide.[3]

Metaxylylglyoxylic acid, (1:3:4), is formed when metaxylylmethylketone is oxidized with potassium permanganate. The ketone is prepared as above from metaxylene, and is a liquid, which smells like peppermint and boils at 227°—228°. The acid is an oily liquid, which solidifies over sulphuric acid to a

[1] Armstrong and Miller, *Ber. Deutsch. Chem. Ges.* xvi. 2255.
[2] *Ann. Chem. Pharm.* cxcv. 284.
[3] Claus and Wollner, *Ber. Deutsch. Chem. Ges.* xviii. 1856.

crystalline mass, melting at 85°. It is oxidized to xylic acid by nitric acid and yields the corresponding aldehyde on distillation.[1]

Orthoxylylglyoxylic acid (1 : 2 : 4). The corresponding ketone is a liquid, which boils at 234° and is immediately oxidized to paraxylic acid by potassium permanganate.[2] A cold, alkaline solution of permanganate converts it into orthoxylylglyoxylic acid, which melts at 92°.[3]

THE DIETHYLBENZENES, $C_6H_4(C_2H_5)_2$.

2434 *Paradiethylbenzene* is formed by the action of sodium on a mixture of parabromethylbenzene and ethyl bromide,[4] as well as on paradibromobenzene and ethyl iodide.[5] It is a liquid, which boils at 178°—179° and yields ethylbenzoic and terephthalic acids on oxidation.

Diethylbenzenes have also been obtained by passing ethyl chloride [6] or ethylene [7] into a mixture of benzene and aluminium chloride, and one at least is present in petroleum from Baku (Markownikow).

When ethylbenzene is heated with aluminium chloride, benzene, paradiethylbenzene and a little metadiethylbenzene are obtained, this being proved by the fact that the product, which boils at 176°—188°, yields terephthalic acid accompanied by a small amount of isophthalic acid on oxidation.[8]

Diethylchlorobenzenes are formed when ethylene is passed into the chlorinated benzenes in the presence of aluminium chloride.[9]

PHENYLENEDI-ACETIC ACIDS, $C_6H_4(CH_2.CO_2H)_2$.

2435 *Orthophenylenedi-acetic acid.* When orthoxylylene bromide is shaken up with an alcoholic solution of potassium cyanide, a considerable rise of temperature occurs and *orthoxylylene cyanide*,

[1] Claus and Strommenger, *Ber. Deutsch. Chem. Ges.* xix. 230.
[2] Claus and Claussen, *ibid.* xix. 232.
[3] Buchka and Irish, *ibid.* xx. 1766.
[4] Fittig and König, *Ann. Chem. Pharm.* cxliv. 285.
[5] Aschenbach, *ibid.* ccxvi. 212.
[6] Allen and Underwood, *Bull. Soc. Chim.* xl. 100.
[7] Balsohn, *ibid.* xxxi. 540.
[8] Anschütz, *Ann. Chem. Pharm.* cxxxv. 189.
[9] Istrati, *Ann. Chim. Phys.* [6] vi. 413 and 482.

$C_6H_4(CH_2.CN)_2$, is obtained. It forms crystals, melting at 59°—60° and is decomposed into a tarry mass on heating with alkalis, but is converted by boiling with dilute sulphuric acid into orthophenylenedi-acetic acid, which crystallizes from hot water in fine needles, melting at 150°.[1]

Metaphenylenedi-acetic acid is formed by heating the corresponding cyanide with alcoholic potash and crystallizes from hot water in concentrically grouped needles, which melt at 170° and can be distilled without decomposition. The cyanide, a crystalline substance, which melts at 28°—29°, is prepared by heating metaxylylene bromide with an aqueous solution of potassium cyanide.[2]

Paraphenylenedi-acetic acid or *Paraxylenedicarboxylic acid.* The nitril of this acid, *paraxylylene cyanide*, has been prepared from the corresponding chloride and bromide; it crystallizes from alcohol in needles and from ether in long, three-sided prisms, melting at 98°. On heating with hydrochloric acid or alcoholic potash, it is converted into the acid, which crystallizes from hot water in long, flat needles, melts at 244° and volatilizes without decomposition.[3]

THE METHYLPROPYLBENZENES, $C_6H_4\begin{matrix}CH_3\\C_3H_7\end{matrix}$.

2436 In the year 1841 Gerhardt and Cahours discovered cymene (*cymène*), $C_{10}H_{14}$, together with *cuminol*, $C_{10}H_{12}O$, the aldehyde of cumic acid, in Roman cumin oil (*Cuminum cyminum*),[4] and stated that it was identical with *camphene*, which Dumas had obtained by the distillation of camphor, $C_{10}H_{16}O$ with phosphorus pentoxide, and which was then further investigated by Delalande.[5]

Cymene was then detected in other ethereal oils, but it was assumed that the hydrocarbon which occurs in nature is isomeric with that prepared from camphor.

Fittig, Schäffer and König then obtained *propyltoluene*, $C_3H_7.C_6H_4.CH_3$, by the action of sodium on a mixture of propyl

[1] Baeyer and Pape, *Ber. Deutsch. Chem. Ges.* xvii. 447.
[2] Kipping, *Journ. Chem. Soc.* 1888, i. 41.
[3] Biedermann, *Ber. Deutsch. Chem. Ges.* v. 702; Klippert, *ibid.* ix. 1766; Kipping, *loc. cit.*
[4] *Ann. Chem. Pharm.* xxxviii. 70 and 101. [5] *Ibid.* xxxviii. 342 and 345.

bromide and bromotoluene, which agrees in its properties with cymene and, like the latter, yields paratoluic acid and terephthalic acid on oxidation. They did not however consider themselves justified in asserting the identity of this synthetical hydrocarbon with the cymene from cumin oil.

As already mentioned, cymene occurs in association with cuminol; the cumic acid, which is obtained from the latter, decomposes on distillation with lime into carbon dioxide and cumene, C_9H_{12}, which, as found by the chemists mentioned above, differed from propylbenzene and very probably contained the isopropyl group, so that cymene itself, they concluded, was probably isopropyltoluene.[1]

Attempts to prepare the latter by the action of sodium on a mixture of isopropyl iodide and bromotoluene were unsuccessful, the iodide not being attacked.[2]

The products of oxidation of cymene were now investigated by Buliginsky and Erlenmeyer,[3] and also by Dittmar and Kekulé,[4] who found among them the acids already mentioned and also acetic acid, which could only be derived under these circumstances from a normal propyl derivative. Beilstein and Kupfer,[5] and Fittica,[6] then proved that natural cymene is identical with that prepared from camphor, and the last-named chemist prepared parapropyltoluene from pure parabromotoluene and found that it is also identical with the hydrocarbons in question.

Nencki and Ziegler, on the other hand, observed that cymene, administered internally, appears in the urine as cumic acid,[7] which certainly contains the isopropyl group, while Kraut found that cumin alcohol, prepared from cuminaldehyde, is reduced to cymene by heating with zinc dust[8] and was confirmed by Jacobsen, who prepared isopropyltoluene synthetically and showed that it differs from cymene. In order to explain the change from cumin alcohol into cymene "an intermolecular change of the propyl-group"[9] must be assumed.

That this actually occurs is proved by the examples already mentioned and those which follow.

If the one side-chain in a derivative of para-isopropylmethylbenzene, as for example, cumin alcohol or its chloride, be

[1] *Ann. Chem. Pharm.* cxlix. 334.
[2] Hoogewerff, *ibid.* cxlix. 337; Jacobsen, *Ber. Deutsch. Chem. Ges.* xii. 429.
[3] *Ann. Chem. Pharm.* cxl. 137.
[4] *Ibid.* clxii. 337.
[5] *Ibid.* clxx. 282 and 290.
[6] *Ibid.* clxxii. 303.
[7] *Ber. Deutsch. Chem. Ges.* v. 749.
[8] *Ann. Chem. Pharm.* cxcii. 224.
[9] *Ber. Deutsch. Chem. Ges.* xii. 429.

reduced to methyl, the isopropyl- changes into the normal propyl-group.

If, on the other hand, the methyl group in cymene is oxidized to carboxyl, the inverse change takes place, the normal propyl-group being converted into the iso-group; in this way cymene is thus not only converted into cumic acid by the organism, but also by agitation with air and caustic soda.

These and other observations led Widman to enunciate the following law:

"When a methyl or a carboxyl group is present in a benzene derivative in the para-position with respect to a propyl-group, the latter tends to assume the normal constitution in the presence of the methyl, the iso-constitution in the presence of the carboxyl group."[1]

2437 Cymene occurs together with cuminol in Roman cumin oil and in that of the seeds of *Cicuta virosa*,[2] and together with a terpene, $C_{10}H_{16}$, and thymol, $C_3H_7.C_6H_3(OH)CH_3$, in oil of thyme (*Thymus vulgaris*)[3] and oil of ajowan (*Ptychotis ajowan*),[4] which have been used as spices and as medicine in India, Persia, and Egypt from very early times. It also forms a constituent of oil of pepper-wort (*Satureja hortensis*),[5] of oil of wild thyme (*Thymus serpyllum*),[6] of eucalyptus oil (*Eucalyptus globulus*),[7] and of essence of resin.[8]

Cymene also occurs in old oil of turpentine, $C_{10}H_{16}$, and is formed from this in considerable quantity by treatment with sulphuric acid, which has an oxidizing action.[9] It is formed still more freely, together with ether, when oil of turpentine is heated with ethyl sulphate.[10]

Oil of turpentine combines with bromine to form the dibromide, $C_{10}H_{16}Br_2$, which decomposes on distillation,[11] or better, by heating with aniline,[12] into hydrobromic acid and cymene.

[1] *Ber. Deutsch. Chem. Ges.* xix. 251, 2769, 2781.
[2] *Ann. Chem. Pharm.* cviii. 386. [3] Lallemand, *ibid.* cii. 119.
[4] Haines, *Quart. Journ. Chem. Soc.* viii. 289; *Journ. Prakt. Chem.* lxviii. 430; H. Müller, *Ber. Deutsch. Chem. Ges.* ii. 130; Landolph, *ibid.* vi. 936.
[5] Jahns, *ibid.* xv. 816.
[6] Febve, *Compt. Rend.* xcii. 1290.
[7] Faust and Homeyer, *Ber. Deutsch. Chem. Ges.* vii. 1429.
[8] *Ibid.* xix. 1969.
[9] Riban, *Bull. Soc. Chim.* xix. 242; xx. 101; xxi. 4; Wright, *Journ. Chem. Soc.* 1873, 700; *Chem. News*, xxix. 41; Richter and Orlowsky, *Ber. Deutsch. Chem. Ges.* vi. 1257; Tilden, *Journ. Chem. Soc.* 1878, i. 80.
[10] Bruère, *Compt. Rend.* xc. 1428.
[11] Barbier, *Ber. Deutsch. Chem. Ges.* v. 215.
[12] Oppenheim, *ibid.* v. 94 and 628.

Iodine exerts a very violent action upon oil of turpentine, so that even ignition can occur when large amounts are added. If it be carefully added in small quantities and the solution heated for some time, cymene is formed according to the following equation :[1]

$$C_{10}H_{16} + I_2 = C_{10}H_{14} + 2HI.$$

Several of the isomerides of oil of turpentine behave in the same manner, readily losing two atoms of hydrogen and passing into cymene.

Camphor, $C_{10}H_{16}O$, is also readily converted into cymene by elimination of water, which may be effected by heating with phosphorus pentoxide, phosphorus pentachloride or phosphorus pentasulphide.

In order to prepare cymene, camphor is distilled with phosphorus pentasulphide :[2]

$$5C_{10}H_{16}O + P_2S_5 = 5C_{10}H_{14} + 5H_2S + P_2O_5.$$

The product is purified by washing with caustic potash and rectification.

A better yield is obtained by mixing equal molecules of camphor and phosphorus pentoxide, heating gently until the reaction commences, when the flame must be removed, and pouring off the cymene from the metaphosphoric acid. It is then heated once more with phosphorus pentoxide and distilled two or three times over sodium.[3]

It may be prepared from oil of turpentine by adding 4 per cent. of phosphorus trichloride and passing in one molecule of chlorine for every molecule of the hydrocarbon present, the temperature being kept at 25° and not being allowed to rise above this point; the product is then washed with water, dried and distilled over sodium.[4]

Cymene is a strongly refractive, aromatic smelling liquid, which boils at 175° and has the sp. gr. 0·791 at 0°. It gives a characteristic absorption spectrum by means of which it can be detected in essential oils.[5]

It combines with aluminium bromide to form the compound $3C_{10}H_{14} + Al_2Br_6$, a reddish brown, transparent liquid, which

[1] Kekulé, *Ber. Deutsch. Chem. Ges.* vi. 437.
[2] Pott, *ibid.* ii. 121.
[3] Fittica, *Ann. Chem. Pharm.* clxxii. 307.
[4] Naudin, *Bull. Soc. Chim.* xxxvii. 111.
[5] Hartley, *Journ. Chem. Soc.* 1880, i. 676.

reacts very energetically with bromine, pentabromotoluene and isopropyl bromide being formed, which are therefore also formed when bromine is gradually added to cymene containing a little aluminium, the compound just described being continuously formed and decomposed.[1]

It forms a similar compound with aluminium chloride (Gustavson), and on heating with the chloride decomposes with formation of toluene and high boiling condensation products.[2]

2438 *Addition products of cymene.* Oil of turpentine and its isomerides, which are converted into cymene by the loss of two hydrogen atoms, must be considered as *dihydrocymenes.* They will however be subsequently described.

Hexhydrocymene, $C_{10}H_{20}$, occurs in essence of resin and boils at 171°—173° (Renard).

Halogen substitution products of cymene. When chlorine is passed into boiling cymene, *cymyl chloride,* $C_3H_7.C_6H_4.CH_2Cl$, is formed, together with two isomeric compounds, one of which is unattacked by alcoholic potash, while the other, $C_3H_6Cl.C_6H_4.CH_3$, is converted by it into allyltoluene,[3] $C_3H_5.C_6H_4.CH_3$.

Orthochlorocymene, $C_3H_7.C_6H_3Cl.CH_3(CH_3 : Cl : C_3H_7 = 1 : 2 : 4)$, was first prepared by Kekulé and Fleischer from carvacrol, $C_3H_7.C_6H_3(OH)CH_3$, by the action of phosphorus pentachloride,[4] and has also been obtained by Gerichten by the action of chlorine on cymene in the presence of iodine.[5] It is an almost odourless, colourless liquid, which boils at 208°—211° and is converted into metachloroparatoluic acid by oxidation.

Metachlorocymene (1 : 3 : 4) is formed by the action of phosphorus chloride on thymol, and is a liquid which boils at 213°—214° and is oxidized by nitric acid to a mixture of chlorocumic, orthochloroparatoluic and chloroterephthalic acids.[6]

Orthobromocymene, $C_3H_7.C_6H_3Br.CH_3$, is obtained when bromine is allowed to act upon cymene in the presence of iodine, and is a liquid which smells like cymene, boils at 228°—229°, and yields *a*-bromoparatoluic acid on oxidation.[7]

Metabromocymene is formed, together with thymyl phosphate,

[1] Gustavson, *Bull. Soc. Imp. Nat. de Moskou,* 1886, Nr. 2.
[2] Anschütz, *Ann. Chem. Pharm.* ccxxxv. 191.
[3] Errera, *Gaz. Chim. Ital.* xiv. 283.
[4] *Ber. Deutsch. Chem. Ges.* vi. 1090.
[5] *Ibid.* x. 1249.
[6] Carstanjen, *Journ. Prakt. Chem.* [2], iii. 63 ; Gerichten, *Ber. Deutsch. Chem. Ges.* xi. 364 ; Fileti and Crosa, *ibid.* xx. Ref. 139.
[7] Landolph, *ibid.* v. 267 ; see also Fittica, *Ann. Chem. Pharm.* clxxii. 310.

when thymol is heated with phosphorus pentabromide (Fileti and Crosa):

$$4\ C_{10}H_{13}.OH + PBr_5 = C_{10}H_{13}Br + PO(OC_{10}H_{13})_3 + 4HBr.$$

Its sulphonic acid is formed by the action of bromine on cymene-orthosulphonic acid. When this is heated with steam in presence of sulphuric acid, metabromocymene is obtained as a liquid boiling at 232°—233° (Fileti and Crosa).[1]

Cymene-orthosulphonic acid, $C_3H_7.C_6H_3(SO_3H)CH_3$. Cahours and Gerhardt, as well as Delalande, obtained a sulphonic acid by the action of fuming sulphuric acid on cymene, which was then investigated by Sieveking,[2] Beilstein and Kupffer[3] and Jacobsen.[4] Further investigations then proved that a small quantity of an isomeric acid is also formed.[5]

The orthosulphonic acid is the chief product and crystallizes from dilute sulphuric acid in tablets containing two molecules of water. On fusion with potash it is converted into carvacrol.

Cymenemetasulphonic acid can readily be separated from the ortho-acid by means of the barium salt, since that of the latter crystallizes in plates, which are only slightly soluble in water and have a harsh, bitter taste, while that of the meta-acid is extremely soluble and remains on evaporation as a sweet gelatinous mass. The free acid, obtained from the lead salt, which possesses very similar properties, separates from a very concentrated, syrupy solution in crystalline granules.

Nitrocymene, $C_3H_7.C_6H_3(NO_2)CH_3$, was obtained by Barlow by the action of well-cooled, fuming nitric acid on cymene.[6] According to Landolph[7] and Fittica,[8] it is better to employ nitric acid of sp. gr. 1·4, heated to 50°. It is a yellowish, faintly odorous liquid, which is volatile with steam and is converted into β-nitroparatoluic acid by oxidation. The product of oxidation, according to Widman and Bladin, consists chiefly of paratolylmethylketone (p. 145),[9] in the formation of which the normal propyl group must have passed into the isopropyl form.

[1] Kelbe and Koschnitzky, *Ber. Deutsch. Chem. Ges.* xix. 1730.
[2] *Ann. Chem. Pharm.* cvi. 257.
[3] *Ibid.* clxx. 287.
[4] *Ber. Deutsch. Chem. Ges.* xi. 1058.
[5] Claus and Cratz, *ibid.* xiii. 901; Spica, *ibid.* xiv. 653; Claus, *ibid.* xiv. 2139.
[6] *Ann. Chem. Pharm.* xcv. 245.
[7] *Ber. Deutsch. Chem. Ges.* vi. 937.
[8] *Ann. Chem. Pharm.* clxxii. 314.
[9] *Ber. Deutsch. Chem. Ges.* xix. 584.

Another substance is also formed, which crystallizes in needles or small plates, melts at 125° and is not volatile with steam, which was considered to be an isomeric nitrocymene, until Gerichten showed that this is not the case, since it is converted into paratoluic acid by heating with sulphuric acid or caustic potash solution.[1] According to Holleman, this body is the isonitroso-compound of a diketone and has the following constitution :[2]

$$CH_3.C_6H_4.CO.C(NOH)C(NOH)CO.C_6H_4.CH_3.$$

Metamidocymene or *Thymylamine*, $C_3H_7.C_6H_3(NH_2)CH_3$, was obtained by Widman by converting nitrocuminaldehyde, $C_3H_7.C_6H_3(NO_2)CHO$, into nitrocumidenechloride by the action of phosphorus chloride, and reducing this with zinc and hydrochloric acid :[3]

$$C_9H_{10}\begin{matrix}CHCl_2\\NO_2\end{matrix} + 10H = C_9H_{10}\begin{matrix}CH_3\\NH_2\end{matrix} + 2H_2O + 2HCl.$$

It is also formed, together with dithymylamine, when thymol or metacymophenol is heated to 350°—360° with zinc bromide ammonia and ammonium bromide.[4] It is an oily, unpleasant smelling liquid, which boils at 230° ; its salts colour pine-wood yellow.

Dithymylamine, $(C_3H_7.C_6H_3.CH_3)_2NH$, is an oily liquid which has a pleasant aromatic odour, and boils at 340°—345°.

Orthamidocymene or *Carvacrylamine* was prepared by Lloyd from orthocymophenol or carvacrol as an oily liquid, which has a not unpleasant odour and boils at 241°—242°. It is probably identical with the *cymidine*, which Barlow obtained by the reduction of nitrocymene and described as a yellowish oil, boiling at 250°, the hydrochloride of which colours pine-wood yellow.

Dicarvacrylamine is an extremely pleasant smelling oil, which boils at 344°—348° (Lloyd).

Azocymene, $(C_3H_7.C_6H_3.CH_3)_2N_2$, was obtained by Schumow by diluting cymene with 3 parts of glacial acetic acid, cooling the mixture with ice and salt, carefully adding concentrated nitric acid and pouring the product into water. The precipitated nitrocymene, which is not described, is then converted

[1] *Ber. Deutsch. Chem. Ges.* xi. 1092.
[2] *Ibid.* xx. Ref. 373.
[3] *Ibid.* xv. 166.
[4] Rachel Lloyd, *ibid.* xx. 1254.

into azocymene by reduction with sodium amalgam. It crystallizes from benzene in ruby-red, rhombic tablets, melting at 86°.[1]

2439 *Metacymophenol* or *Thymol*, $C_3H_7.C_6H_3(OH)CH_3$, Neumann, court apothecary in Berlin, observed in 1719 that crystals, which he thought were camphor, are deposited from oil of thyme, but Brown explained that these had long been known in England under the name of *Sal volatile thymi*, and are different from camphor. This compound was more fully investigated by Lallemand and named thymol.[2] It also occurs, as previously mentioned, in Ajowan oil, and was investigated by Haines[3] and Stenhouse.[4] It has long been known in India, as in the preparation of the oil it separates from the aqueous distillate in crystals and is sold in the bazaars under the name of Ajwain-ka-phyl or flowers of Ajowan.[5] It was also obtained from essential oil of monarda (*Monarda punctata*) by Arppe, and was identified as thymol by Stenhouse and Gerhardt.[6]

It is prepared from oil of thyme or oil of Ajowan, from which it can be obtained by fractional distillation. It is however more usual to extract it by agitation with caustic soda solution and precipitate it from the solution by hydrochloric acid. It is then purified by recrystallization from alcohol, or better, glacial acetic acid.

It forms large monosymmetric or asymmetric crystals, which smell like thyme, have a sharp, burning taste, and melt at 50°.[7] According to Lallemand it boils at 230°, while Stenhouse states the boiling point as 222°. On distillation with phosphorus pentasulphide it yields cymene (Fittica), and is decomposed into metacresol and propylene by heating with phosphorus pentoxide.[8]

It yields a violet-red colouring matter, $C_{30}H_{36}N_2O_4$, on treatment with sulphuric acid and nitrous acid (Liebermann, *see* Pt. I. p. 176). Owing to its strong antiseptic properties it is employed in medicine, since it has a more powerful action than phenol and is at the same time less corrosive and poisonous.

[1] *Ber. Deutsch. Chem. Ges.* xx. 3, 218.
[2] *Compt. Rend.* xxxvii. 498 ; xxxviii. 1022 ; xliii. 357 ; *Ann. Chem. Pharm.* ci. 122 ; cii. 119.
[3] *Quart. Journ. Chem. Soc.* viii. 289.
[4] *Ann. Chem. Pharm.* xciii. 269 ; xcviii. 307.
[5] Haines ; Stenhouse ; *Pharmacographia*, 2nd Edit. 303.
[6] *Trait. Chim. Org.* iii. 610.
[7] Menschutkin, *Beilstein's Organ. Chem.* 1048.
[8] Engelhardt and Latschinow, *Zeitschr. Chem.* 1869, 621.

As a phenol it forms salts, ethers, and ethereal salts :

	Melting-point.	Boiling-point.
Thymyl methyl ether,[1] $C_{10}H_{13}OCH_3$ . . .	—	216·7°
Thymyl ethyl ether,[2] $C_{10}H_{13}OC_2H_5$	—	222°
Thymyl ethenyl ether,[3] $(C_{10}H_{13}O)_2C_2H_4$ . .	99°	—
Thymyl phosphate,[4] $(C_{10}H_{13})_3PO_4$	59°	—
Thymyl silicate,[5] $(C_{10}H_{13})_4SiO_4$	48°	450°
Thymyl ethyl carbonate,[6] $C_{10}H_{13}(C_2H_3)CO_3$	—	259°—262°
Dithymyl carbonate, $(C_{10}H_{13})_2CO_3$	48°	—
Thymyl acetate,[7] $C_{10}H_{13}OC_2H_3O$	—	244·7°
Thymyl benzoate,[8] $C_{10}H_{13}OC_7H_5O$	32°	—

Thiothymol, $C_3H_7.C_6H_3(SH)CH_3$, is formed, together with cymene, by the action of phosphorus pentasulphide on thymol, and is a liquid which has a characteristic pungent odour and boils at 230°—231°. It readily combines with mercuric oxide to form the mercaptide, $(C_{10}H_{13}S)_2Hg$, which separates from alcohol in greenish, rhombohedral forms.[9]

2440 *Orthocymophenol* (1 : 2 : 4). Schweizer discovered that cumin oil contains in addition to carvene, $C_{10}H_{16}$, an oxygenous compound, which is converted when the oil is distilled with potassium, caustic potash, iodine or glacial phosphoric acid, into *carvacrol*, a thick, oily liquid, which has a persistent, pungent taste and a characteristic, unpleasant odour, its vapour attacking the lungs very violently.[10]

Claus obtained an oily liquid, accompanied by other products, by the distillation of camphor with iodine, which resembles creosote in both taste and smell, and was therefore named by him *camphor creosote*.[11] Schweizer then repeated this research and convinced himself that carvacrol and camphor creosote are identical.[12]

The oxygenated constituent of cumin oil was first isolated by Völckel, who named it *carvol*, and gave it the formula $C_{30}H_{21}O_3$, assigning to carvacrol the formula $C_{30}H_{20}O_2$(C = 6 ; O = 8).[13]

[1] Paternò, *Bull. Soc. Chim.* xxv. 32.
[2] Jungfleisch, *Zeitschr. Chem.* 1865, 532.
[3] Paternò.
[4] Engelhardt and Latschinow, *Zeitschr. Chem.* 1869, 44.
[5] Hertkorn, *Ber. Deutsch. Chem. Ges.* xviii. 1693.
[6] Richter, *Journ. Prakt. Chem.* [2], xxvii. 503.
[7] Paternò.
[8] Stohmann, *Journ. Prakt. Chem.* [2], xxxvi. 7.
[9] Fittica, *Ann. Chem. Pharm.* clxxii. 325.
[10] *Journ. Prakt. Chem.* xxiv. 271.
[11] *Ibid.* xxv. 266.
[12] *Ibid.* xxvi. 118.
[13] *Ann. Chem. Pharm.* lxxxv. 246.

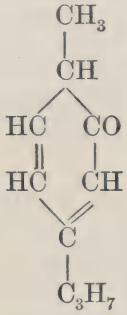
Varrentrapp subsequently showed that carvol has the composition $C_{20}H_{14}O_2$, and Gerhardt then suggested that it is isomeric with carvacrol.[1]

Pott[2] and Hugo Müller[3] obtained an *oxycymol* or *cymophenol* by fusing cymenesulphonic acid with caustic potash, and this was shown by Kekulé and Fleischer to be also identical with carvacrol and camphor creosote.[4]

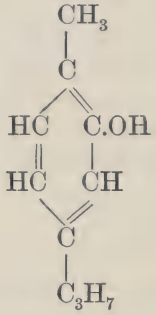
The same substance occurs in smaller quantity in *Thymus serpyllum*, accompanied by thymol and cymene. It forms about 30 per cent. of oil of pepper-wort (*Satureja hortensis et montana*) and from 50—80 per cent. of Spanish oil of hops or Cretan oil of marjoram (*Origanum hirsutum et creticum*), from which it can be readily separated.[5] A good yield is also obtained by fusing sodium cymenesulphonate with three parts of caustic potash.[6]

Its formation from the isomeric carvol, which will be subsequently described, is especially worthy of note. The constitution of these compounds is expressed by the following formulae :

Carvol.



Carvacrol.



The latter, therefore, stands in the same relation to the former as phoroglucinol to triketohexhydrobenzene, which, however, is not known in the free state (Pt. IV. p. 518).

When carvol is heated with metaphosphoric acid or crystallized phosphoric acid, it is converted into carvacrol, so much heat being evolved that an explosion may occur; it is therefore

[1] *Trait. Chim. Organ.* iii. 615.
[2] *Ber. Deutsch. Chem. Ges.* ii. 121.
[3] *Ibid.* ii. 130.
[4] *Ibid.* vi. 1087.
[5] Jahns, *ibid.* xv. 816; Huller, *Compt. Rend.* xciv. 132.
[6] Jacobsen, *Ber. Deutsch. Chem. Ges.* xi. 1060.

better to employ crude cumin oil and subsequently separate the carvacrol from the carvene by means of caustic potash solution (Kekulé and Fleischer).

According to Lustig, the action is not so violent and it is most advantageous to heat a mixture of 50 grms. of carvol and 50 grms. of cumin oil with 12 grms. of glacial phosphoric acid to boiling for 3—4 hours, pour off the thick liquid and isolate the carvacrol by fractional distillation.[1]

Properties.—It is a somewhat viscid liquid, which, according to Müller, has an aromatic odour, resembling that of Russian leather, while Jacobsen states that it has a faint, characteristic odour, which becomes pungent when the liquid is heated. It boils at 237° and solidifies on cooling to crystals, which melt at about 1°. Its alcoholic solution is coloured green by ferric chloride (Jahns). On distillation with phosphorus pentasulphide, it yields cymene and is decomposed by heating with phosphorus pentoxide into propylene and a cresol (Kekulé and Fleischer), which is the ortho-compound, while on heating with phosphorus oxychloride it is converted into *cymophenyl phosphate*, $(C_{10}H_{13})_3PO_4$, which crystallizes from benzene in prisms or tablets and melts at 75° (Kreysler).

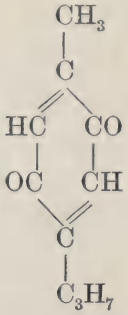
	Boiling-point.
Cymophenyl methyl ether,[2] $C_{10}H_{13}OCH_3$ . .	216·8°
Cymophenyl ethyl ether,[3] $C_{10}H_{13}OC_2H_5$ . . .	235°
Cymophenyl acetate, $C_{10}H_{13}O.C_2H_3O$ . . .	245·8°

Thiocymene or *Thiocarvacrol*, $C_3H_7.C_6H_3(SH)CH_3$, is obtained in a similar manner to thiothymol and is also formed, together with cymene, by the distillation of carvol or camphor with phosphorus pentasulphide and by the action of nascent hydrogen on cymenesulphonic chloride.[4] It is a liquid, which has a characteristic aromatic odour, boils at 235°—236° and forms a mercaptide, $(C_{10}H_{13}S)_2Hg$, which crystallizes from alcohol in stellate groups of needles.[5]

2441 *Thymoquinone*, $C_3H_7.C_6H_2O_2.CH_3$, was first obtained by Lallemand by the oxidation of thymol with sulphuric acid and manganese dioxide and termed *thymoïl*.[6] It may be prepared in

[1] *Ber. Deutsch. Chem. Ges.* xix. 11.
[2] Pisati and Paternò, *ibid.* viii. 71.
[3] Lustig, *loc. cit.*
[4] Flesch, *ibid.* vi. 478; Rodenberg, *ibid.* vi. 669; Fleischer and Kekulé, *loc. cit.*
[5] Fittica, *Ann. Chem. Pharm.* clxxii. 325.
[6] *Ibid.* cii. 119.

a similar manner from carvacrol,[1] its formation being explained by the following constitutional formula:



It is only slightly soluble in water, readily in alcohol, and crystallizes in lustrous, yellow tablets, which have a penetrating aromatic odour, melts at 45·5°, boils at 232°, and is readily volatile with steam.[2]

If its ethereal solution be allowed to stand in the light, it is converted into *polythymoquinone*, which crystallizes in long, light yellow, odourless needles, which melt at 200°—201° and sublime at a higher temperature, but do not volatilize with steam. It is not reduced by sulphurous acid but is converted into thymoquinol by boiling with hydriodic acid and red phosphorus, by heating the alcoholic solution with zinc and hydrochloric acid or by distillation over zinc dust.[3]

Thymoquinol, $C_3H_7.C_6H_2(OH)_2CH_3$, which was called *thymoïlol* by Lallemand, is formed by the reduction of the quinone with sulphurous acid. It crystallizes from hot water in four-sided, colourless, lustrous prisms, melting at 139·5°.

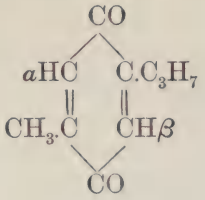
Dimethylthymoquinol, $C_3H_7.C_6H_2(OCH_3)_2CH_3$, forms the chief constituent of the ethereal oil of Arnica root (p. 5). It boils at about 235°, is resolved into methyl iodide and thymoquinol by heating with hydriodic acid.[4]

Thymoquinhydrone, $C_3H_7.C_6H_2(OH)_2CH_3 + C_3H_7.C_6H_2O_2.CH_3$, is formed by the combination of the quinone with the quinol, and crystallizes in lustrous black needles.

Thymoquinone contains two hydrogen atoms, α and β, of

[1] Kekulé and Fleischer, *Ber. Deutsch. Chem. Ges.* vi. 1087.
[2] Carstanjen, *Journ. Prakt. Chem.* [2], iii. 54.
[3] Liebermann, *Ber. Deutsch. Chem. Ges.* x. 2177; Liebermann and Hinski, *ibid.* xviii. 3193.
[4] Sigel, *Ann. Chem. Pharm.* clxx. 363.

unequal value and therefore gives rise to two series of mono-substitution products.



a-Chlorothymoquinone, $C_{10}H_{11}ClO_2$. When thymoquinone is brought into hydrochloric acid saturated at 0°, *a-chlorothymoquinone*, $C_{10}H_{13}ClO_2$, is formed; it crystallizes from petroleum-ether in silky needles, melting at 70°; and is oxidized by distillation with ferric chloride to the quinone. The latter is a yellow liquid, which cannot be distilled without decomposition, but is volatile with steam.

β-Chlorothymoquinone is formed by the action of chlorine on the corresponding bromine compound and is also an oily liquid. The corresponding quinol resembles it closely in appearance.

β-Bromothymoquinone, $C_{10}H_{11}BrO_2$. Thymoquinone is not converted into the *a*-bromoquinol by solution in hydrobromic acid, but the *β*-compound is formed. This crystallizes in colourless needles, melting at 53°, while the corresponding quinone forms lustrous yellow plates, melting at 45°.

a-Chloro-β-bromothymoquinone, $C_{10}H_{10}ClBrO_2$, is formed by the careful bromination of the *a*-chloroquinone and crystallizes from hot alcohol in small, yellow plates, which melt at 87°. It is not affected by sulphurous acid, but is reduced by free hydroxylamine to the quinol, which is also formed by the action of hydrochloric acid on the *β*-bromoquinone and of hydrobromic acid on the *a*-chloroquinone; it crystallizes in needles, melting at 63°.

β-Chloro-a-bromothymoquinone has been prepared from the *β*-chloroquinone and forms reddish yellow plates, melting at 78°, while its quinol crystallizes in needles, which melt at 56°.[1]

2442 *Hydroxythymoquinone*, $C_{10}H_{11}(OH)O_2$. Thymoquinone reacts with dimethylamine in alcoholic solution in the following manner:

$$2C_{10}H_{12}O_2 + NH(CH_3)_2 = C_{10}H_{12}(OH)_2 + C_{10}H_{11}O_2N(CH_3)_2.$$

Dimethylamidothymoquinone is precipitated from this solution by water in violet-black, oily drops, and is converted by heating

[1] Schniter, *Ber. Deutsch. Chem. Ges.* xx. 1316.

with hydrochloric acid into hydroxythymoquinone. This substance crystallizes from hot water in yellow needles or small plates, which melt at 166°—167°.[1]

Diamidothymoquinone, $C_{10}H_{10}(NH_2)_2O_2$. If the hydroxyquinone be boiled with aniline and alcohol, *hydroxythymoquinoneanilide*, $C_{10}H_{10}(OH)O_2NH(C_6H_5)$, is formed and crystallizes in dark violet needles, which have a metallic lustre and melt at 134°—135°. On heating with saturated alcoholic ammonia, it is converted into diamidothymoquinone, which crystallizes in blue-black needles with a metallic lustre and sublimes on heating without previously melting.[2]

Thymoquinonoxime or *Nitrosothymol*, $C_3H_7.C_6H_2O(NOH)CH_3$, is formed when a solution of thymol in caustic potash is treated with potassium nitrite and sulphuric acid.[3] It may also be obtained by the combination of hydroxylamine with thymoquinone.[4] It is slightly soluble in water, readily in alcohol, and crystallizes from chloroform in small, yellow needles, which melt at 160°. Its alkali salts crystallize in long, dark yellow needles. It is oxidized by potassium ferricyanide in alkaline solution to *nitrothymol*, $C_3H_7C_6H_2(OH)(NO_2)CH_3$, and this is also formed when an aqueous solution of thymosulphonic acid is heated with nitric acid.[5] It crystallizes in thin, yellow needles, which show a bluish fluorescence and melt at 140°.

Nitrosothymol is reduced by the action of tin and hydrochloric acid to *amidothymol*, $C_3H_7.C_6H_2(OH)(NH_2)CH_3$, which is very unstable in the free state and is converted by bromine,[6] ferric chloride,[7] or chromic acid [8] into thymoquinone, while bleaching powder acts upon it in hydrochloric acid solution with production of *thymoquinone chlorimide*, $C_3H_7.C_6H_2O(NOCl)CH_3$, a yellow liquid, which possesses a penetrating odour and decomposes on heating, but is volatile with steam (Andresen).

Polythymoquinonoxime, $[C_3H_7.C_6H_2O(NOH)CH_3]_x$, is formed by the combination of polythymoquinone with hydroxylamine and forms a crystalline powder, which detonates when rapidly heated and is reduced to amidothymol by tin and hydrochloric acid.

[1] Schulz, *Ber. Deutsch. Chem. Ges.* xvi. 898.
[2] Anschütz and Leather, *Ann. Chem. Pharm.* ccxxxvii. 114.
[3] R. Schiff, *Ber. Deutsch. Chem. Ges.* viii. 1500.
[4] Goldschmidt and Schmid, *ibid.* xvii. 2060.
[5] Liebermann, *ibid.* x. 612.
[6] Andresen, *Journ. Prakt. Chem.* [2], xxiii. 172.
[7] Armstrong, *Ber. Deutsch. Chem. Ges.* x. 297.
[8] Liebermann and Ilinski, *ibid.* xviii. 3193.

Polythymoquinonedioxime, $[C_3H_7.C_6H_2(NOH)_2CH_{3x}]$, is obtained, when the polyquinone is heated with hydroxylamine, as a difficultly soluble, white powder, which is converted by reduction into *diamidocymene hydrochloride*, $C_3H_7.C_6H_2(NH_2)_2CH_3(ClH)_2$. This salt crystallizes in needles, which readily decompose with formation of ammonium chloride and are oxidized to thymoquinone by ferric chloride (Liebermann and Ilinski).

Nitrosocarvacrol has been prepared from carvacrol and crystallizes in yellowish prisms, melting at 153°. It is converted by oxidation into *nitrocarvacrol*, which forms yellowish needles, melting at 77°—78° and yields amidocarvacrol, which is likewise very unstable in the free state, on reduction.[1]

2443 *Orthopropylmethylbenzene* or *Orthocymene*, $C_3H_7.C_6H_4CH_3$, is obtained by the action of sodium on a mixture of orthobromotoluene and propyl iodide. It is an aromatic smelling liquid, which boils at 181°—182°[2] and behaves towards potassium permanganate in the cold in the same manner as orthomethylethylbenzene, the phthalic acid produced being accompanied by a considerable amount of terephthalic acid (p. 144).

Metapropylmethylbenzene or *Metacymene* has been prepared in a similar manner from metabromotoluene; it boils at 176°—177·5°.[3] Like the ortho-compound, it yields two sulphonic acids with sulphuric acid.

Para-isocymene, $(CH_3)_2CH.C_6H_4.CH_3$, was obtained by Jacobsen by heating parabromocumene and methyl iodide with sodium in the presence of ether and a few drops of acetic ether, without which the reaction only proceeds very slowly.

It is a liquid, which has a similar smell to cymene, does not solidify at −20°, boils at 171°—172°, and has a sp. gr. of 0·8702 at 0°. On heating to 90°—100° with sulphuric acid, two sulphonic acids are obtained: the one which is formed in preponderating amount, yields a barium salt, $(C_{10}H_{13}SO_3)_2Ba + H_2O$, which crystallizes in hair-like needles and is more than twice as soluble in water as barium cymenesulphonate. The barium salt of the other acid forms an opaque, readily soluble, semi-crystalline mass.[4]

Meta-isocymene, $(CH_3)_2CHC_6H_4.CH_3$, occurs in resin spirit,[5] and among the products formed by the action of zinc chloride[6]

[1] Paternò and Canzoneri, *Ber. Deutsch. Chem. Ges.* xii. 383.
[2] Claus and Hansen, *ibid.* xiii. 867. [3] Claus and Stüsser, *ibid.* xiii. 899.
[4] *Ibid.* xii. 429.
[5] Kelbe, *Ann. Chem. Pharm.* ccx. 1; Renard, *Ann. Chim. Phys.* [6], i. 249.
[6] Armstrong and Miller, *Ber. Deutsch. Chem. Ges.* xvi. 2255.

or phosphorus pentoxide[1] on camphor, and is formed when toluene is heated with isopropyl iodide and aluminium chloride (Kelbe). It is a strongly refractive liquid, which boils at 174°—176° and smells like cymene. It is oxidized by dilute nitric acid to metatoluic acid, and by chromic acid or potassium permanganate to isophthalic acid. It is violently attacked by chlorine and bromine, but substitution only takes place in the side chains, even in the cold.

α-Bromometa-isocymene, $(CH_3)_2CH.C_6H_3BrCH_3$(1 : 4 : 3), is formed when a solution of hydrobromic acid is mixed with one of *α*-meta-isocymenesulphonic acid. It is a strongly refractive liquid, which smells somewhat like roses and boils at 225° (Kelbe and Czarnowski.) It is oxidized to *α*-bromometatoluic acid by nitric acid.

β-Bromometa-isocymene (1 : 6 : 3). In the preparation of the preceding compound, a bromosulphonic acid is simultaneously formed, which yields the *β*-substitution compound on heating with concentrated hydrochloric acid. This substance has a faint aromatic odour, boils at 224°, and is slowly oxidized to *β*-bromometatoluic acid by nitric acid.

On further oxidation, both these bromometa-isocymenes yield bromisophthalic acid, melting at 283°.[2]

Dibromometa-isocymene, $(CH_3)_2CH.C_6H_2Br_2.CH_3$ (1 : 4 : 6 : 3), is formed by heating the solution of the sulphonic acid with bromine, and is a liquid, which has a faint odour and boils at 272°—273°.

Meta-isocymenesulphonic acid, $(CH_3)_2CH.C_6H_3(SO_3H)CH_3$, is obtained by dissolving the hydrocarbon in hot sulphuric acid in two modifications, which may be separated by means of their barium salts. That of the *α*-acid, which is the chief product, crystallizes with one molecule of water in large, nacreous plates, which are only slightly soluble in water, while the salt of the *β*-acid is readily soluble and contains eight molecules of water.[3]

Meta-isocymophenol or *Cymenol*, $(CH_3)_2CH.C_6H_3(OH)CH_3$, has been prepared from the *α*-sulphonic acid; it is a strongly refractive liquid, which boils at 231°, and has an odour resembling thymol and simultaneously wood smoke, and a vapour which causes violent coughing. Its aqueous solution is coloured

[1] Spica, *Gaz. Chim. Ital.* xii. 487, 543.
[2] Kelbe, *Ber. Deutsch. Chem. Ges.* xv. 39.
[3] Kelbe and Czarnowski, *Ann. Chem. Pharm.* ccxxxv. 27.

a faint violet by ferric chloride. On fusion with caustic potash it yields *α*-hydroxyisophthalic acid and para-isopropylphenolcarboxylic acid (p. 310), its constitution being thus determined.

Cymenyl methyl ether, $C_3H_7(CH_3)C_6H_3.OCH_3$, is an oily liquid, which has an aromatic odour and a burning taste and boils at 217°.[1]

Cymenyl benzoate, $C_3H_7(CH_3)C_6H_3.O.CO.C_6H_5$, crystallizes from petroleum-spirit in monosymmetric prisms, melting at 73° (Kelbe).

Nitrometa-isocymene, $(CH_3)_2CH.C_6H_3(NO_2)CH_3$, is an oily liquid, which has a spicy odour and yields nitrotoluic acid, melting at 214°, on oxidation.

Amidometa-isocymene or *Meta-isocymidine*, $(CH_3)_2CH.C_6H_3(NH_2)CH_3$, is a strongly refractive liquid, which has an odour resembling that of aniline and boils at 232°—233°.[2]

CYMYL-COMPOUNDS.

2444 *Cymyl alcohol* or *Cumin alcohol*, $(CH_3)_2CH.C_6H_4.CH_2OH$, was obtained by Kraut by the action of alcoholic potash on cuminaldehyde. It is an oily, faintly aromatic smelling liquid, which has a burning taste, boils at 246·6°, and has a sp. gr. of 0·9775 at 15°. It is reduced to cymene by continued boiling with zinc dust (p. 288).[3]

Cymyl chloride, $(CH_3)_2CH.C_6H_4.CH_2Cl$, is formed by the action of hydrochloric acid on the alcohol and is a liquid, which boils at 230°[4] and is reduced to cymene by zinc and hydrochloric acid. A cymyl chloride, which probably contains the normal propyl group, is obtained by the action of chlorine on boiling cymene. According to Errera, two other isomeric chlorides are also formed (p. 291); if the mixture, which boils at 225°—229°, be boiled with water and lead nitrate, cuminaldehyde $(CH_3)_2CH.C_6H_4.CHO$, is obtained.[5]

Cymyl ethyl ether, $C_3H_7.C_6H_4.CH_2OC_2H_5$, was obtained by Errera, together with allyltoluene, by boiling the chlorides with alcoholic potash, as a liquid, boiling at 227°.

[1] Jesurun, *Ber. Deutsch. Chem. Ges.* xix. 1413.
[2] Kelbe and Warth, *Ann. Chem. Pharm.* ccxxi. 157.
[3] *Ibid.* xcii. 66; cxcii. 224.
[4] Rossi, *ibid. Suppl.* i. 139; Paternò and Spica, *Gaz. Chim. Ital.* ix. 397.
[5] *Ibid.* xiv. 277.

Dicymyl ether or *Cumin ether*, $(C_3H_7.C_6H_4.CH_2)_2O$, is formed when a few drops of dilute sulphuric acid are added to the alcohol and the mixture heated to 200° and then distilled. It may also be obtained by the action of sodium cymylate on cymyl chloride, and is a liquid which has a sweet smell, boils at about 350°, and is partially decomposed by distillation into cymene and cuminaldeyde, the decomposition being almost complete after several redistillations.[1]

Cymyl acetate, $C_3H_7.C_6H_4.CH_2OC_2H_3O$, was prepared by Czumpelik by heating the impure chloride obtained from cymene with potassium acetate. It is a liquid, which boils at 236° and smells like rose-wood oil.[2]

Cymylamine, $C_3H_7.C_6H_4.CH_2.NH_2$, is formed, together with the secondary and tertiary bases, by heating the chloride with ammonia (Rossi). Czumpelik obtained it by the action of zinc and hydrochloric acid on thio-cuminamide, $C_3H_7.C_6H_4.CS.NH_2$ (p. 307),[3] and Raab by distilling cymylcarbimide, prepared from cymyl chloride and silver cyanate, with caustic potash.[4]

It is however best prepared by the action of sodium amalgam and acetic acid on cuminaldoxime, which is described below.[5] It is a liquid, which has an ammoniacal odour and boils at 226°—227°.

Cymyl mustard oil, $C_3H_7.C_6H_4.CH_2.NCS$, has a faint but distinct smell of mustard, and decomposes on distillation (Raab).

THE PROPYLBENZOIC ACIDS.

2445 *Cuminol* or *Cuminaldehyde*, $(CH_3)_2CH.C_6H_4.CHO$, occurs, as previously mentioned, in the ethereal oil of the Roman cumin and the seeds of the hemlock accompanied by cymene, from which it is probably formed by oxidation (Widman). It is prepared from Roman cumin oil by agitating the portion which boils above 190° with a saturated solution of sodium sulphite, washing the granular crystalline precipitate, which has separated after twenty-four hours, with ether and decomposing it by dis-

[1] Fileti, *Gaz. Chim. Ital.* xiv. 469.
[2] *Ber. Deutsch. Chem. Ges.* iii. 480.
[3] *Ibid.* ii. 185.
[4] *Ibid.* viii. 1148 ; x. 52.
[5] Goldschmidt and Gessner, *ibid.* xx. 2413.

tillation with sodium carbonate solution or dilute sulphuric acid.[1]

Cuminol is an oily liquid, which has the smell of Roman cumin oil, boils at 236·5°[2] and readily oxidizes in the air. It produces a violet-red colouration in a solution of fuchsin which has been decolourized by sulphurous acid.[3] Its derivatives resemble those of benzaldehyde.

Cuminaldoxime, $(CH_3)_2CH.C_6H_4.CH(NOH)$, forms crystals, which melt at 52°.[4]

Metanitrocuminol, $(CH_3)_2CH.C_6H_3(NO_2)CHO$, is formed by the action of a cooled mixture of nitric and sulphuric acids on the aldehyde and crystallizes in oblique, sulphur-yellow prisms, melting at 54°.[5]

Orthonitrocuminol has been obtained by the oxidation of orthonitrocumenylic acid, $(CH_3)_2CH.C_6H_3(NO_2)CH{=}CH.CO_2H$, with potassium permanganate. It is an oily liquid, and yields a blue colouring matter on heating with acetone and caustic soda, which is undoubtedly di-isopropylindigo.[6]

Para-isopropylbenzoic acid, $(CH_3)_2CH.C_6H_4.CO_2H$. Chevallier discovered an acid in an old sample of Roman cumin oil which had become sour, which resembled succinic acid and was undoubtedly cuminic acid.[7] It was then prepared by Gerhardt and Cahours by allowing cuminol to drop on to fused caustic potash, and is also formed, according to these chemists, by the oxidation of cuminol in the air, especially in presence of an alkali, and by the action of potassium chromate and sulphuric acid and other oxidizing agents.[8]

In order to prepare it, Roman cumin oil is allowed to drop on to an equal weight of fused caustic potash contained in an iron retort, the mass allowed to cool as soon as the evolution of hydrogen ceases, water added and the unattacked oil distilled off. The cuminic acid is separated from the residue with hydrochloric acid and purified by conversion into the calcium or magnesium salt.[9]

It may also be readily obtained by agitating 6 parts of

[1] Kraut, *Ann. Chem. Pharm.* xcii. 66.
[2] H. Kopp, *ibid.* xciv. 317; Meyer, *Ber. Deutsch. Chem. Ges.* x. 150.
[3] Schmidt, *ibid.* xiv. 1850.
[4] Westenberger, *ibid.* xvi. 2994.
[5] Lippmann and Strecker, *ibid.* xii. 76.
[6] Einhorn and Hess, *ibid.* xvii. 2019.
[7] Kraut, *Gmelin's Org. Chem.* vii. 143.
[8] *Ann. Chem. Pharm.* xxxviii. 72.
[9] Beilstein and Kuppfer, *ibid.* clxx. 301.

cuminol with 30 parts of caustic soda solution of sp. gr. 1·25, and adding a solution of 10 parts of potassium permanganate in 250 parts of water, with constant agitation. After a few hours, a little alcohol is added in order to reduce any excess of permanganic acid, the manganese oxide being then filtered off and the cuminic acid precipitated with hydrochloric acid.[1] It is obtained synthetically by the action of carbon dioxide on a mixture of bromocumene and sodium.[2]

It is scarcely soluble in cold, only slightly in hot water and crystallizes from alcohol in asymmetric tablets, which melt at 116·5° and readily sublime in long needles, which have an acid taste and a characteristic faint odour of bugs.

It volatilizes with steam and is oxidized to terephthalic acid by chromic acid and to hydroxyisopropyl-benzoic acid, $(CH_3)_2C(OH)C_6H_4.CO_2H$, by potassium permanganate. On distillation with lime it decomposes into cumene and carbon dioxide and when internally administered appears unaltered in the urine, while cymene is converted into cuminic acid in the human organism[3] and chiefly into cuminuric acid in that of the dog.[4]

Its salts have been investigated by Gerhardt and Cahours, and by Beilstein and Kupffer.

Ethyl cuminate, $(CH_3)_2CH.C_6H_4.CO.C_2H_5$, is a liquid, which smells like apples and boils at 240°.

2446 *Cumoyl chloride*, $(CH_3)_2CH.C_6H_4.COCl$, is a mobile liquid, boiling at 256°—258°,[5] which is well fitted to serve as the starting point in the preparation of the cuminic ethers and other derivatives.

Cuminic anhydride, $(C_3H_7.C_6H_4.CO)_2O$, is a thick, oily liquid, which deposits crystals when preserved for a long time.[6]

Cuminamide, $(CH_3)_2CH.C_6H_4.CO.NH_2$, crystallizes from hot water in lustrous tablets or long needles, which are insoluble in cold water.[7] It may be prepared synthetically from *urea chloride*, $ClCO.NH_2$ (a substance which is obtained when ammonium chloride is heated in a current of carboxyl chloride and forms compact needles, melting at 50°), by bringing this into contact

[1] Meyer and Rosicki, *Ber. Deutsch. Chem. Ges.* xi. 1790; *Ann. Chem. Pharm.* ccxix. 243.

[2] R. Meyer, *Journ. Prakt. Chem.* [2] xxxiv. 93.

[3] Nencki and Ziegler, *Ber. Deutsch. Chem. Ges.* v. 750; Gerichten, *ibid.* xi. 369.

[4] Jacobsen, *ibid.* xii. 1512.

[5] Cahours, *Ann. Chem. Pharm.* lxx. 45.

[6] Gerhardt, *ibid.* lxxxvii. 77.

[7] Field, *ibid.* lxv. 49; Gerhardt, *ibid.* lxxxvii. 167; Gerhardt and Chiozza, *ibid.* lxxxvii. 299.

with cumene and carbon disulphide, gradually adding aluminium chloride and finally heating the mixture:

$$(CH_3)_2CH.C_6H_5 + ClCO.NH_2 = (CH_3)_2CH.C_6H_4.CO.NH + HCl.$$

It melts at 153·5° (Fileti) and is converted into cuminic acid by boiling with caustic potash solution. Several other aromatic acids have been prepared by this reaction.[1]

Thiocuminamide, $(CH_3)_2CH.C_6H_4.CS.NH_2$, is obtained by passing sulphuretted hydrogen into an alcoholic, ammoniacal solution of cumonitril; it forms needles, which are soluble in hot alcohol.[2]

Cumonitril, $(CH_3)_2CH.C_6H_4.CN$, is formed by heating the amide (Field) and by the action of cyanogen bromide on potassium cuminate:[3]

$$C_3H_7.C_6H_4.CO_2K + CNBr = C_3H_7.C_6H_4.CN + CO_2 + KBr.$$

It is also obtained, together with the amide,[4] by heating cuminic acid with potassium thiocyanate[5] (Pt. IV. p. 197).

It is an aromatic smelling liquid, which has a burning taste and boils at 243°—244°.

Cuminuric acid, $(CH_3)_2CH.C_6H_4.CO.NHCH_2.CO_2H$, was prepared by Cahours by the action of cumoyl chloride on silver amido-acetate,[6] and was found by Jacobsen in the urine of dogs after the administration of cymene. It crystallizes from hot water in large, iridescent plates, which melt at 168° and are decomposed into cuminic acid and amido-acetic acid by heating with hydrochloric acid to 120°.

Orthonitrocuminic acid, $(CH_3)_2CH.C_6H_3(NO_2)CO_2H$ (4 : 2 : 1), was obtained by Widman by the oxidation of *orthonitrocumenyl-acrylic acid*, $(CH_3)_2CH.C_6H_3(NO_2)C_2H_2.CO_2H$, with chromic acid or potassium permanganate. It is very readily soluble in alcohol, but with difficulty in petroleum-spirit, and crystallizes from acetic acid of 50 per cent. in slightly oblique, lustrous, colourless tablets, which melt at 99°.[7]

Metanitrocuminic acid (4 : 3 : 1) is formed by the action of fuming nitric acid on cuminic acid,[8] and by the oxidation of

[1] Gattermann and Schmidt, *Ber. Deutsch. Chem. Ges.* xx. 858.
[2] Czumpelik, *ibid.* ii. 185.
[3] Cahours, *Ann. Chem. Pharm.* cviii. 320.
[4] Fileti, *Ber. Deutsch. Chem. Ges.* xx. Ref. 138.
[5] Letts, *ibid.* vi. 674.
[6] *Ann. Chem. Pharm.* cix. 31.
[7] *Ber. Deutsch. Chem. Ges.* xix. 269.
[8] Cahours, *Ann. Chem. Pharm.* lxix. 243.

nitrocuminol with chromic acid.[1] It crystallizes from nitric acid or alcohol in monosymmetric prisms, melting at 158°. It changes in the sunlight to a red, amorphous substance, which also possesses acid properties.[2]

Orthamidocuminic acid, $(CH_3)_2CH.C_6H_3(NH_2)CO_2H$, was prepared by Widman from the nitro-acid by reduction with ammonia and ferrous sulphate. It crystallizes in long tablets or quadratic plates, which melt at 93°—94°.

Metamidocuminic acid is formed by the reduction of meta-nitrocuminic acid with ammonium sulphide or ammonia and ferrous sulphate, and crystallizes in brownish needles, melting at 129°.[3]

2447 *Orthocuminic acid* or *Ortho-isopropylbenzoic acid* is obtained when the potassium or barium salt of cumene-orthosulphonic acid is fused with sodium formate. It is insoluble in cold water, separates from alcohol or ether in an indistinctly crystalline mass, volatilizes with steam, sublimes when carefully heated and decomposes at a higher temperature without previously melting. It is not attacked by aqueous chromic acid solution even on heating, while a solution of chromium trioxide in acetic acid oxidizes it to carbon dioxide and water, and alkaline potassium permanganate converts it into phthalic acid.[4]

Parapropylbenzoic acid, $C_3H_7.C_6H_4.CO_2H$, has been obtained by Paternò and Spica as a product of the oxidation of propyl-isopropylbenzene,[5] and by Körner from paradipropylbenzene.[6] R. Meyer has also prepared it by the action of carbon dioxide on a mixture of sodium and parabromopropylbenzene.[7] It crystallizes from hot water in very lustrous plates, which consist of microscopic, monosymmetric prisms, and separates from alcohol in more compact crystals of the same form, which melt at 140° and readily sublime in long, broad needles. It is oxidized by potassium permanganate to terephthalic acid (R. Meyer).

Orthonitroparapropylbenzoic acid, $C_3H_7.C_6H_3(NO_2)COOH$, is formed by the oxidation of orthonitroparapropylcinnamic acid, $C_3H_7.C_6H_3(NO_2)C_2H_2.CO_2H$, with chromic acid and potassium permanganate and crystallizes from alcohol in rhombic tablets, melting at 156°—157·5°.[8]

[1] Lippmann and Strecker, *Ber. Deutsch. Chem. Ges.* xii. 76.
[2] Paternò and Fileti, *ibid.* ix. 81.
[3] Cahours, *Ann. Chem. Pharm.* cix. 10; Paternò and Fileti, *Ber. Deutsch. Chem. Ges.* vii. 81; Lippmann and Lange, *ibid.* xiii. 1660.
[4] Claus and Schulte, *ibid.* xix. 3012.
[5] *Ibid.* x. 1746. [6] *Ibid.* xi. 1863. [7] *Journ. Prakt. Chem.* [2] xxxiv. 101.
[8] Widman, *Ber. Deutsch. Chem. Ges.* xix. 276.

Orthopropylbenzoic acid is obtained by heating phthalylpropionic acid to 200° with hydriodic acid and amorphous phosphorus:

$$C_6H_4\begin{cases} C{=}C(CH_3)CO_2H \\ >O \\ CO \end{cases} + 4HI =$$

$$C_6H_4\begin{cases} CH_2.CH_2.CH_3 \\ CO.OH \end{cases} + CO_2 + 2I_2.$$

It crystallizes from dilute alcohol in small plates, which melt at 58°.[1]

PROPYLHYDROXYBENZOIC ACIDS.

2448 *Orthohydroxycuminic acid*, $(CH_3)_2CH.C_6H_3(OH)CO_2H$ (4 : 2 : 1). Jacobsen, by fusing para-isocymenesulphonic acid, which is formed in preponderating amount in the sulphonation of cymene, with potash, obtained *hydroxycuminic acid*, melting at 88°,[2] while isohydroxycuminic acid,[3] melting at 93°, was formed by gently heating carvacrol, the two acids resembling each other very closely. They are, indeed, obviously identical, since the normal propyl is converted into the iso-group by the oxidation of carvacrol. The same acid is therefore obtained by the action of nitrous acid on orthamidocuminic acid [4] and by the addition of hydrogen to propenylsalicylic acid,[5] $C_3H_5.C_6H_3(OH)CO_2H$. It separates from hot water in flat needles or plates, which melt at 96°, readily volatilize with steam, give a reddish violet colouration with ferric chloride and decompose into metacumophenol and carbon dioxide on heating with hydrochloric acid.

Metahydroxycuminic acid (4 : 3 : 1), was obtained by Barth, who named it *thymoxycuminic acid*, by fusing thymol with caustic potash.[6] It is also formed by the action of nitrous acid on metamidocuminic acid,[7] and when the potassium salt of thymylsulphuric acid or thymylphosphoric acid is oxidized with alkaline potassium permanganate (Heymann and Königs).

[1] Gabriel and Michael, *Ber. Deutsch. Chem. Ges.* xi. 104.
[2] *Ibid.* xii. 429.
[3] *Ibid.* xi. 1058.
[4] Widman, *ibid.* xix. 252 and 270.
[5] Heymann and Königs, *ibid.* xix. 3304; xx. 2390.
[6] *Ibid.* xi. 1569.
[7] Cahours, *loc. cit.*; Lippmann and Lange, *loc. cit.*

It crystallizes from hot water in long, thin needles, which melt at 143°. Ferric chloride produces an opalescence in the dilute, aqueous solution, but a precipitate in one of greater concentration. On continued fusion with caustic potash, it is converted into hydroxyterephthalic acid, while hydrochloric acid has no action upon it even at 200°.

Para-isopropylphenolcarboxylic acid (5 : 2 : 1) is formed by the action of carbon dioxide and sodium on paracumophenol and crystallizes in nacreous plates or flat needles, which melt at 120·5° and are much more readily soluble in hot than in cold water. Its aqueous solution is coloured deep bluish violet by ferric chloride.[1]

Ortho-isopropylphenolcarboxylic acid (6 : 2 : 1) has been prepared from orthocumophenol and crystallizes in needles, melting at 71°—72°.[2]

Parapropylphenolcarboxylic acid, $C_3H_7.C_6H_3(OH)CO_2H$ (5 : 2 : 1), is obtained from parapropylphenol; it melts at 98° and gives a violet colouration with ferric chloride.

Orthopropylphenolcarboxylic acid (3 : 2 : 1) melts at 93°—94°.[3]

HYDROXYPROPYLBENZOIC ACIDS.

2449 *Hydroxyisopropylbenzoic acid,* $(CH_3)_2C(OH)C_6H_4.CO_2H$. This tertiary alcohol-acid is formed, together with a small quantity of terephthalic acid, by the oxidation of an alkaline solution of cuminic acid with potassium permanganate,[4] and also when cymene is heated with a strongly alkaline solution of the same reagent.[5] It is readily soluble in hot water, and crystallizes from a not too concentrated solution in thin, asymmetric prisms, which melt at 155°—156°. It is oxidized by chromic acid to acetylbenzoic acid and terephthalic acid and decomposes into water and propenylbenzoic acid on heating with hydrochloric acid or acetic anhydride.[6]

Hydroxyisopropylsulphobenzoic acid, $(CH_3)_2C(OH)C_6H_3(SO_3H)CO_2H$, is obtained when cymenesulphonic acid or para-iso-

[1] Paternò and Mazzara, *Gaz. Chim. Ital.* viii. 389.
[2] Fileti, *ibid.* xvi. 113.
[3] Spica, *ibid.* viii. 406.
[4] R. Meyer, *Ber. Deutsch. Chem. Ges.* xi. 1283; *Ann. Chem. Pharm.* ccxix. 248.
[5] Bladin and Widman, *Ber. Deutsch. Chem. Ges.* xix. 252 and 583.
[6] Meyer and Rosicki, *ibid.* xi. 1791, 2172; *Ann. Chem. Pharm. loc. cit.*

cymenesulphonic acid is oxidized with potassium permanganate. Its potassium salt, $C_{10}H_{10}SO_6K_2 + 5H_2O$, crystallizes in large, thick, asymmetric tablets.[1]

Hydroxyisopropylmetanitrobenzoic acid, $(CH_3)_2C(OH)C_6H_3(NO_2)CO_2H$, is formed by the oxidation of metanitrocuminic acid or nitrocuminol with potassium permanganate. It crystallizes from hot water in long, transparent, brittle needles, which melt at 190°—191° and become brown in the light.[2]

Hydroxyisopropylmetamidobenzoic acid, $(CH_3)_2C(OH)C_6H_3(NH_2)CO_2H$, is the product of the action of ferrous sulphate on an ammoniacal solution of the nitro-acid. It crystallizes from ether in lustrous prisms, which do not melt below 270° and are readily soluble in water and alcohol.[3]

Hydroxyisopropylorthonitrobenzoic acid crystallizes from ether in oblong tablets and melts at 168°.

Hydroxyisopropylorthamidobenzoic acid forms colourless prisms, melting at 158° and yields a blue fluorescent ethereal solution.[4]

Hydroxyisopropylsalicylic acid, $(CH_3)_2C(OH)C_6H_3(OH)CO_2H$ ($CO_2H : OH = 1 : 2$). The potassium salts of thymylsulphuric and thymylphosphoric acids are converted by oxidation with potassium permanganate into metahydroxycuminic acid, while on the other hand, the corresponding carvacrol derivatives yield hydroxyisopropylsalicylic acid. This substance crystallizes from hot water in large, flat needles, which melt at 130°—135° and are converted by continued heating or by boiling with dilute hydrochloric acid into propenylsalicylic acid, $C_3H_5.C_6H_3(OH)CO_2H$, which is reduced by nascent hydrogen to orthohydroxycuminic acid.[5]

TOLYLPROPIONIC ACIDS, $CH_3.C_6H_4.C_2H_4.CO_2H$.

2450 *Metatolylpropionic acid* is formed by the oxidation of meta-isobutyltoluene, $CH_3.C_6H_4.CH_2CH(CH_3)_2$, with nitric acid and crystallizes from hot water in white needles, which melt at 125° and readily sublime.[6]

[1] Meyer, *Ann. Chem. Pharm.* ccxx. 9.
[2] Widman, *Ber. Deutsch. Chem. Ges.* xv. 2547.
[3] *Ibid.* xvi. 2569.
[4] *Ibid.* xix. 269.
[5] Heymann and Königs, *ibid.* xix. 3304 ; xx. 2390.
[6] Effront, *ibid.* xvii. 2330.

Parapropylpropionaldehyde, $CH_3.C_6H_4.C_2H_4.CHO$, was obtained by Etard from cymene, which combines with chromyl chloride to form *cumidenedichlorochromic acid*, $CH_3.C_6H_4.CH_2.CH_2.CH(OCrCl_2.OH)_2$, a chocolate-brown, crystalline powder, which is decomposed by water with formation of the aldehyde, which he mistook for cuminol.[1] It is a colourless, strongly refractive liquid, which boils at 222°—223°, has a peppermint-like odour and colours fuchsinsulphurous acid violet.

On continued boiling with nitric acid, it is oxidized to para-toluic acid and is converted into terephthalic acid by potassium permanganate.[2]

DIBASIC ACIDS, $C_6H_4\begin{<}{CO_2H}{C_2H_4.CO_2H}$, AND THEIR DERIVATIVES.

2451 *Methylhomophthalic acid.* When homo-orthophthalonitril (p. 152) is treated in well-cooled alcoholic solution with methyl iodide and alcoholic potash, and the mixture then gently heated, *methylhomophthalonitril* is formed:

$$C_6H_4\begin{<}{CN}{CH_2.CN} + CH_3I = C_6H_4\begin{<}{CN}{CH(CH_3)CN} + HI.$$

It forms large, asymmetric crystals, melts at 36°—37°, boils at 284°—286°, and is converted by sulphuric acid into the corresponding imid, which is converted by heating to 200° with hydrochloric acid into methylhomophthalic acid, which separates from hot water as a crystalline powder, melting at 146°—147°.[3]

Hydrocinnamorthocarboxylic acid is formed by the combination of hydrogen with cinnamocarboxylic acid, $C_6H_4(CO_2H)CH{=}CH.CO_2H$, and crystallizes from hot water in long, lustrous needles, melting at 165°—166°.[4]

Benzhydrylacetocarboxylic acid, $CO_2H.C_6H_4.CH(OH)CH_2CO_2H$. The lactone of this acid is formed by the action of sodium amalgam and water on phthalylacetic acid:

$$C_6H_4\begin{<}{CO}{>O\ C{=}CH{-}CO_2H} + 2H = C_6H_4\begin{<}{CO}{>O\ CH{-}CH_2{-}CO_2H}.$$

[1] *Ann. Chim. Phys.* [5] xxii. 259.
[2] Richter and Schüchner, *Ber. Deutsch. Chem. Ges.* xvii. 1391.
[3] Gabriel, *ibid*, xx. 2499.
[4] Gabriel and Michael, *ibid.* x. 2199.

This latter substance is readily soluble in hot water and alcohol, and crystallizes with one molecule of water in lustrous needles, which become anhydrous at 100°, and melt at 150°—151°. It is a monobasic acid, but yields salts of the dibasic benzhydrylacetocarboxylic acid, which does not exist in the free state, with strong alkalis. These salts change at a temperature of 220°—240° into those of cinnamocarboxylic acid, while inversely, this acid is converted by fusion into the isomeric lactone :[1]

$$C_6H_4\begin{cases}CO.OH\\CH{=}CH{-}CO.OH\end{cases} = C_6H_4\begin{cases}CO\\>O\\CH{-}CH_2.CO.OH\end{cases}.$$

Opianylacetic acid, $(CH_3O)_2C_6H_2\begin{cases}CO_2H\\CH(OH)CH_2.CO_2H\end{cases}$, is also unknown in the free state. Its lactone, *meconinacetic acid* is formed by heating opianic acid with malonic acid, glacial acetic acid and sodium acetate.

$$(CH_3O)_2C_6H_2\begin{cases}CO.OH\\CHO\end{cases} + CH_2\begin{cases}CO_2H\\CO_2H\end{cases} =$$

$$(CH_3O)_2C_6H_2\begin{cases}CO\\>O\\CH{-}CH_2.CO_2H\end{cases} + CO_2 + H_2O.$$

It crystallizes from hot water in lustrous needles, which melt at 167°. On boiling with baryta water, barium opianylacetate is formed and yields meconinacetic acid again when decomposed by an acid. If the latter be heated with hydriodic acid, *normeconinacetic acid* is formed :

$$(HO)_2C_6H_2\begin{cases}CO\\>O\\CH{-}CH_2.CO_2H\end{cases}$$

This crystallizes from hot water in long tablets, melting at 228°.[2]

[1] *Ber. Deutsch. Chem. Ges.* x. 1558 and 2199.
[2] Liebermann and Kleemann, *ibid.* xix. 2290.

METHYLPROPENYLBENZENE AND ITS DERIVATIVES.

2452 *Methylpropenylbenzene*, $CH_3.C_6H_4.CH{=}CH.CH_3$. This hydrocarbon, which is also known as *allyltoluene*, is formed when the product obtained by chlorinating boiling cymene is heated with alcoholic potash. It is a liquid, boiling at 192°, which is oxidized by potassium permanganate to paratoluic acid and behaves in a similar manner to styrolene, since it changes when preserved or kept in contact with calcium chloride into the amorphous *meta-allyltoluene*, which is re-converted into allyltoluene on distillation. The latter undergoes condensation on heating with hydrobromic acid, *di-allyltoluene*, a liquid, which boils at 350°, being formed.[1]

Metamethylcinnamic acid, $CH_3.C_6H_4.CH{=}CH.CO_2H$, which has also been named *tolylacrylic acid*, is obtained by heating metatolualdehyde with acetic anhydride and sodium acetate and crystallizes from boiling water in silky needles, which melt at 110°—111°. Its ammonium salt gives an egg-yellow precipitate with ferric chloride, similar to that which is given by ammonium cinnamate.[2]

Homo-umbelliferon, $CH_3.C_6H_2(OH)\begin{cases} O\text{——}CO \\ \quad\quad\;\; | \\ CH{=}CH \end{cases}$, is formed when equal molecules of orcinol and malic acid are heated with sulphuric acid. It is insoluble in water, readily soluble in alcohol, and crystallizes from acetone in yellowish tablets, melting at 248°, the solution of which in alkalis or sulphuric acid has a blue fluorescence. On fusion with potash, it yields orcylaldehyde and acetic acid.[3]

Propenylbenzoic acid, $C_3H_5.C_6H_4.CO_2H$, is prepared by heating hydroxyisopropylbenzoic acid with dilute hydrochloric acid :

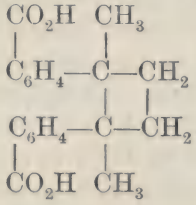
$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C(OH)C_6H_4.CO_2H = \begin{matrix} CH_3 \\ CH_2 \end{matrix}\!\!>C{-}C_6H_4.CO_2H + H_2O.$$

It is insoluble in cold and only slightly soluble in hot water, readily soluble in alcohol, crystallizing from dilute alcohol in

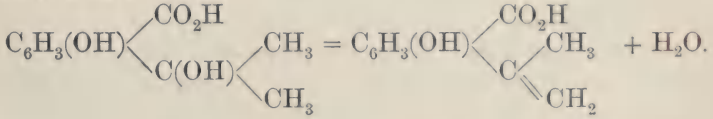
[1] Errera, *Gaz. Chim. Ital.* xiv. 277 and 504.
[2] Bornemann, *Ber. Deutsch. Chem. Ges.* xvii. 1474 ; xx. 1382.
[3] Pechmann and Welsh, *ibid.* xvii. 1646.

small plates or needles, which have a satin lustre and melt at 160°—161°. It is reconverted into cuminic acid by sodium amalgam and water.

Isopropenylbenzoic acid is formed when stronger hydrochloric acid is employed in the above reaction and is insoluble in water. It crystallizes from hot alcohol in stellate groups of microscopic needles, which melt at 255°—256°. It is unattacked by water and sodium amalgam, but is converted into cuminic acid by heating with hydriodic acid and phosphorus. It probably stands in a similar relation to propenylbenzoic acid as does isatropic to atropic acid (p. 233) and has perhaps the following constitution :[1]



Propenylsalicylic acid, $C_3H_5.C_6H_3(OH)CO_2H$, is best obtained by heating hydroxyisopropylsalicylic acid with dilute hydrochloric acid :



It is also only slightly soluble in hot water and crystallizes from carbon disulphide in fine needles, which melt at 145°—146°. It sublimes at 150° with slight decomposition, is volatile with steam and gives a deep reddish violet colouration with ferric chloride. Sodium amalgam and water convert it into ortho-hydroxycuminic acid.[2]

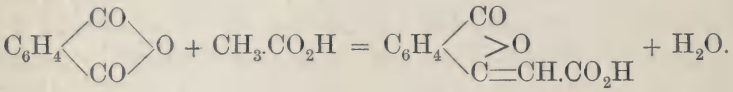
Eugetinic acid, $C_3H_5.C_6H_2(OH)(OCH_3)CO_2H$, is formed by the action of carbon dioxide and sodium on eugenol and crystallizes from water in long, thin prisms, which melt at 124° and decompose when heated for some time into carbon dioxide and eugenol (p. 197). Its aqueous solution is coloured deep blue by ferric chloride.[3]

Methyleugetinic acid, $C_3H_5.C_6H_2(OCH_3)_2CO_2H$. The ethyl

[1] R. Meyer and Rosicki, *Ann. Chem. Pharm.* ccxix. 270.
[2] Heymann and Königs, *Ber. Deutsch. Chem. Ges.* xix. 3304 ; xx. 2390.
[3] Scheuch, *Ann. Chem. Pharm.* cxxv. 17.

ether of this acid is formed when methylbromeugenol is treated with sodium and ethyl chlorocarbonate. The free acid forms broad, yellow crystals, which melt at 180° and are difficultly soluble in water.[1]

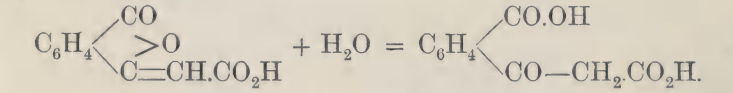
2453 *Phthalylacetic acid* is obtained when phthalic anhydride is heated with sodium acetate and acetic anhydride:



It separates from alcohol, in which it is only slightly soluble, in distorted crystals, while it crystallizes from glacial acetic acid, or better nitrobenzene, in broad needles,[2] which melt above 260° and decompose at 276° with evolution of gas.[3]

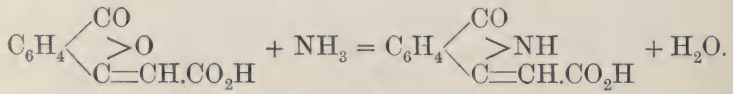
Cinnamocarboxylic acid, $CO_2H.C_6H_4.CH{=}CH.CO_2H$. The formation of this acid from benzhydrylacetocarboxylic acid has already been mentioned (p. 313); it crystallizes from hot water in fine needles, which melt at 173°—175° and are thus converted into the lactone of benzhydrylacetocarboxylic acid.

Benzoylacetocarboxylic acid is formed by the action of alkalis on phthalylacetic acid:



It crystallizes from hot water in vitreous needles, which melt at 90° and on further heating or on boiling with water are resolved into carbon dioxide and acetophenonecarboxylic acid.

Phthalimidylacetic acid is the product of the action of ammonia on phthalylacetic acid:

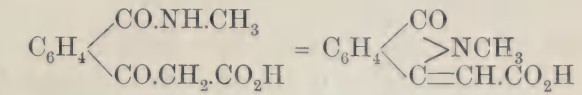


It crystallizes from hot water in silky needles, which melt at 200° with evolution of gas.[4]

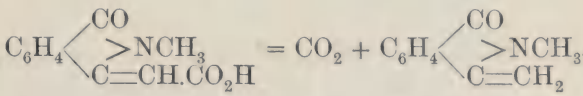
[1] Wassermann, *Ber. Deutsch. Chem. Ges.* x. 237; *Compt. Rend.* lxxxviii. 1206.
[2] Gabriel and Michael, *Ber. Deutsch. Chem. Ges.* x. 391 and 1551.
[3] Roser, *ibid.* xvii. 2619.
[4] Gabriel and Michael, *loc. cit.*; Roser, *Ber. Deutsch. Chem. Ges.* xvii. 2623; Gabriel, *ibid.* xviii. 2451.

Phthalmethimidylacetic acid. When phthalylacetic acid is treated with a solution of methylamine, the liquid being well cooled during the operation, *methylamidobenzoylacetocarboxylic acid* is formed :

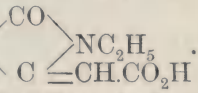
This substance forms a crystalline powder consisting of small prisms and is converted into phthalmethimidylacetic acid by cold sulphuric acid :



The body separates out when the solution is allowed to stand for some time and is then poured into water, and crystallizes from alcohol in silky needles, which decompose on heating into carbon dioxide and *methylenephthalmethimidine ;*



It is left behind as a syrup and soon solidifies to a hard crystalline mass, which melts even with the heat of the hand and volatilizes with steam, its vapour having a pungent odour. If the clear distillate be extracted with ether and the latter evaporated, the imidine is obtained in transparent, pointed prisms, which, however, soon become clouded and soft, while needles of a substance which is not volatile with steam are deposited if the aqueous solution be allowed to stand.

Phthalmethimidylacetic acid,  . Ethylamine reacts with phthalylacetic acid differently from methylamine, two molecules of each combining to form a substance $C_{23}H_{24}N_2O_5$, with elimination of carbon dioxide and water. This body crystallizes from lukewarm alcohol in needles, which melt and froth up at 129°. It is converted by cold sulphuric acid into the acid, which crystallizes from alcohol in yellow needles, melting at 180° with evolution of gas.

In the formation of this acid one molecule of water and one of *methylenephthalmethimidine* are withdrawn from the original

condensation product and the same imidine is also formed when this body is heated above its melting point, carbon dioxide and water being eliminated. It is an oily liquid, which smells like fresh carrots and is volatile with steam.

Propylamine behaves towards phthalylacetic acid in a similar manner to ethylamine, while secondary and tertiary amines simply form salts.

Methylenephthalphenimidine. When aniline and phthalylacetic acid are brought together, carbon dioxide is evolved and if the reaction be completed on the water-bath and the liquid allowed to stand for twenty-four hours, the *anilide of acetophenone-ortho-carboxylic acid*, $C_{15}H_{13}NO_2$, separates out. This body crystallizes from hot alcohol or benzene in large, colourless cubes, melting at 189°—192°, and is decomposed into water and methylene-phthalphenimidine when gradually heated to 230°, aniline being at the same time formed in a secondary reaction:

$$C_6H_4\begin{<}\begin{matrix}CO.NH.C_6H_5\\CO.CH_3\end{matrix} = H_2O + C_6H_4\begin{<}\begin{matrix}CO\\>NC_6H_5.\\C{=}CH_2\end{matrix}$$

Methylenephthalphenimidine crystallizes from alcohol in yellowish prisms, melting at 100°. If the anilide be treated with sulphuric acid, a substance isomeric with the imidine is formed, melting at 265.°[1]

THE BUTYLBENZENES.

2454 *Butylbenzene*, $C_6H_5.CH_2.CH_2.CH_2.CH_3$, is formed by the action of sodium on a mixture of propyl bromide and benzyl bromide,[2] or of butyl bromide and bromobenzene.[3] It is a liquid, which has a very pleasant odour, boils at 180°, and has a sp. gr. of 0·875 at 0° and of 0·8622 at 16°.

α-Isobutylbenzene, $C_6H_5.CH_2CH(CH_3)_2$, is obtained by treating a mixture of bromobenzene and isobutyl bromide[4] or isobutyl iodide,[5] or of benzyl chloride and isopropyl iodide,[6] with sodium.

It is also formed by heating isobutyl alcohol with benzene and

[1] Mertens, *Ber. Deutsch. Chem. Ges.* xix. 2367.
[2] Radziszewski, *ibid.* ix. 260.
[3] Balbiano, *ibid.* x. 296.
[4] Riess, *ibid.* iii. 779.
[5] Wreden and Znatowicz, *ibid.* ix. 1606.
[6] Aronheim and Köhler, *ibid.* viii. 509.

zinc chloride,[1] and by the action of aluminium chloride on a mixture of isobutyl chloride and benzene.[2]

It is a pleasant smelling liquid, which boils at 167·5° and has a sp. gr. of 0·890 at 15° (Radziszewski).

a-Isobutylpara-iodobenzene, $C_6H_4I.C_2H_3(CH_3)_2$, was obtained by Pahl from the amido-compound by means of the diazo-reaction. It forms a radiating crystalline mass which has an aromatic odour and boils at 255°—256°. It is oxidized by nitric acid to para-iodobenzoic acid.[3]

Isobutylphenol, $C_6H_4(OH)C_2H_3(CH_3)_2$, is formed by heating phenol with isobutyl alcohol and zinc chloride,[4] as well as by the action of nitrous acid on isobutylamidobenzene. It crystallizes in needles, melting at 99°, boils at 236°,[5] has a faint, not unpleasant odour and gives no colouration with ferric chloride. On heating with phosphorus pentoxide it is resolved into phenol and isobutylene.

Isobutylparamidobenzene, $C_6H_4(NH_2)C_2H_3(CH_3)_2$, is obtained by heating aniline hydrochloride with isobutyl alcohol to 230°[6] and also by heating isobutylphenol with zinc bromide-ammonia and ammonium bromide to 320°—330°.[7] It is a faintly odorous liquid, boiling at 235°—237°; its hydrochloride is stable in the air and crystallizes in fine tablets.

Nitramido-isobutylbenzene, $C_6H_3(NO_2)(NH_2)C_4H_9$, forms reddish yellow crystals, melts at 106·5° and is converted by reduction into *diamido-isobutylbenzene*, $C_6H_3(NH_2)_2C_4H_9$, which crystallizes from hot water in thick, micaceous tablets or plates, melts at 97·5° and boils at 280°—282°. Its general behaviour shows that the amido-groups are in the ortho-position.[8]

Phenisobutyl mustard oil, $C_6H_4(NCS)C_2H_3(CH_3)_2$, crystallizes from petroleum-spirit in needles, melting at 42° and boils at 277° (Pahl).

β-Isobutylbenzene, $C_6H_5.CH(C_2H_5)CH_3$, was obtained by Radziszewski by the action of zinc ethyl on secondary phenylethyl bromide as a liquid, which possesses a characteristic odour, boils at 170°—172° and has a sp. gr. of 0·8726 at 16°.

[1] Goldschmidt, *Ber. Deutsch. Chem. Ges.* xv. 1066 and 1425.
[2] Gossin, *Bull. Soc. Chim.* xli. 446.
[3] Pahl, *Ber. Deutsch. Chem. Ges.* xvii. 1232.
[4] Liebmann, *ibid.* xiv. 1842.
[5] v. Dobrzycki, *Journ. Prakt. Chem.* [2] xxxvi. 390.
[6] Studer, *Ann. Chem. Pharm.* ccxi. 234.
[7] R. Lloyd, *Ber. Deutsch. Chem. Ges.* xx. 1254.
[8] Gelzer, *ibid.* xx. 3253.

ALCOHOLS, $C_6H_5.C_4H_9O$, AND KETONES, $C_6H_8.C_4H_7O$.

2455 *Methylstyrolylcarbinol*, $C_6H_5.C_2H_4.CH(OH)CH_3$, is formed by the action of sodium amalgam on an alcoholic solution of acetocinnamone, $C_6H_5.CH{=}CH.CO.CH_3$, and forms a crystalline mass, melting at 68°.[1]

Methylstyrolylketone, $C_6H_5.C_2H_4.CO.CH_3$, is obtained by boiling benzylaceto-acetic ether with alcoholic potash[2] and also by the distillation of the calcium salts of hydrocinnamic and acetic acids.[3] It is an aromatic smelling liquid, which boils at 235°—236°, readily combines with acid sulphites of the alkalis and is converted by oxidation into benzoic acid.

Ethylbenzylketone, $C_6H_5.CH_2.CO.C_2H_5$, has been prepared from phenylacetyl chloride and zinc ethyl. It boils at 225°—226°, does not combine with the acid sulphites of the alkalis and yields propionic and benzoic acids on oxidation.[4]

Propylphenylketone, $C_6H_5.CO.C_3H_7$, is formed when calcium butyrate and benzoate are heated together,[5] and is also obtained by the action of aluminium chloride on a mixture of benzene and butyryl chloride.[6] It is a pleasant smelling liquid, which boils at 220°—222°, does not form an alkali sulphite-compound and is also oxidized to propionic and benzoic acids by chromic acid.

Isopropylphenylketone, $C_6H_5.CO.CH(CH_3)_2$, boils at 209°—217° and yields acetone and benzoic acids as oxidation products.[7]

PHENYLBUTYRIC ACIDS.

2456 *Phenylbutyric acid*, $C_6H_5.CH_2.CH_2.CH_2.CO_2H$, is formed by the continued action of an excess of sodium amalgam on a hot solution of phenylisocrotonic acid, $C_6H_5.CH{=}CH.CH_2.CO_2H$, kept neutral by the addition of sulphuric acid. It boils at about

[1] Engler and Leist, *Ber. Deutsch. Chem. Ges.* vi. 254.
[2] Ehrlich, *Ann. Chem. Pharm.* clxxxvii. 11.
[3] Jackson, *Ber. Deutsch. Chem. Ges.* xiv. 889.
[4] Popow, *ibid.* v. 500.
[5] Schmidt and Fieberg, *ibid.* vi. 498.
[6] Burcker, *Bull. Soc. Chim.* xxxvii. 4.
[7] Popow, *Ber. Deutsch. Chem. Ges.* vi. 1255.

290°, crystallizes from hot water in long, flat plates, resembling those of benzoic acid, and melts at 47·5°.[1]

Phenylisobutyric acid or *Methylbenzylacetic acid*, $C_6H_5.CH_2.CH(CH_3)CO_2H$, is obtained by heating benzylmethylaceto-acetic ether with concentrated caustic potash, as well as by heating methylbenzylmalonic acid, $CH_3.C(CH_2C_6H_5)(CO_2H)_2$; it is also formed by the combination of hydrogen with phenylcrotonic acid,[2] $C_6H_5.CH{=}C(CH_3)CO_2H$. It crystallizes in plates, is only slightly soluble in cold water, melts at 37° and boils at 272°. When its ammonium salt is heated to 230°, *phenylisobutyramide* is formed; it crystallizes in needles, melting at 109°.

PHENYLHYDROXYBUTYRIC ACIDS.

2457 *Phenylhydroxybutyric acid*, $C_6H_5.CH(OH)CH_2.CH_2.CO_2H$. The phenylisocrotonic acid, which is mentioned above, combines with hydrobromic acid to form phenylbromobutyric acid, which is converted by a dilute solution of sodium carbonate or by boiling with water into *phenylbutyrolactone* $C_6H_5.CH\left\langle\begin{matrix}CH_2.CH_2\\ |\\ O-CO\end{matrix}\right.$, which crystallizes from alcohol in long, flat needles and from carbon disulphide in splendid, six-sided, rhombic tablets, has an aromatic odour, melts at 37° and boils at 306°, but readily sublimes at 100°. If it be boiled with baryta water, the solution well-cooled with ice and then treated with hydrochloric acid, phenylhydroxybutyric acid is precipitated. . The free acid separates from carbon disulphide in flat, transparent crystals, which decompose on heating into water and the lactone (Fittig and Jayne).

Phenylhydroxyisobutyric acid or *Benzylmethylglycolic acid*, $C_6H_5.CH_2.C(CH_3)(OH)CO_2H$, was obtained by Gabriel and Michael by heating the hydrogen sodium sulphite compound of benzylmethylketone in closed vessels with potassium cyanide and alcohol and boiling the solution thus obtained with hydrochloric acid. It crystallizes from benzene in long prisms, which melt at 97°—99° and are readily soluble in hot water and alcohol.[3]

[1] Fittig and Jayne, *Ann. Chem. Pharm.* ccxvi. 107.
[2] Conrad and Bischoff, *ibid.* cciv. 177; Edeleano, *Ber. Deutsch. Chem. Ges.* xx. 616.
[3] *Ber. Deutsch. Chem. Ges.* xii. 814.

KETONIC ACIDS, $C_{10}H_{10}O_3$.

2458 *Benzoylpropionaldehyde*, $C_6H_5.CO.CH_2.CH_2.CHO$, is formed when the compound of propylphenylketone with chromyl chloride (Pt. IV. p. 6) is decomposed with water. It is an aromatic smelling liquid, which boils at about 235° and readily oxidizes to the following compound.[1]

Benzoylpropionic acid, $C_6H_5.CO.CH_2.CH_2.CO_2H$, is the corresponding ketonic acid to the above aldehyde and is formed when a mixture of benzene and succinic anhydride is heated with aluminium chloride,[2] as well as by heating benzoylisosuccinic acid,[3] $C_6H_5CO.C_2H_3.(CO_2H)_2$. It crystallizes from hot water in flat, lustrous needles or plates, which melt at 116° and when more strongly heated are partially converted into a red substance and partly sublime. The action of sodium amalgam on its alkaline solution reduces it to phenylbutyrolactone. Its phenylhydrazone crystallizes in silky needles, which soon change into a yellow resinous mass.

BENZOYLACETONE AND BENZOYLPYRORACEMIC ACID.

2459 *Benzoylacetone*, $C_6H_5.CO.CH_2.CO.CH_3$, is formed, together with acetophenone and benzoic acid, when benzoylacetic acid is boiled with water.[4] It is also a product of the action of sodium ethylate on a mixture of acetone and ethyl benzoate,[5] but it is best prepared by covering sodium ethylate, free from alcohol, with an excess of acetic ether and gradually adding the calculated quantity of acetophenone, the liquid being cooled with ice. The liquid product solidifies after a short time to a thick mass of light yellow crystals of sodium benzoylacetone :

$$C_2H_5.ONa + C_6H_5.CO.CH_3 + C_2H_5.OCO.CH_3 = C_6H_5.CO.CHNa.CO.CH_3 + 2C_2H_5.OH.$$

[1] Burcker, *Compt. Rend.* xciv. 220.
[2] Burcker, *Bull. Soc. Chim.* xxxv. 17 ; Pechmann, *Ber. Deutsch. Chem. Ges.* xv. 889.
[3] Kues and Paal, *ibid.* xviii. 3323 ; see also Bischoff, *ibid.* xix. 95.
[4] Fischer and Kuzel, *ibid.* xvi. 2239 ; Fischer and Bülow, *ibid.* xviii. 2131.
[5] Claisen, *ibid.* xx. 655.

The mass is triturated with ether and filtered, the residue being dissolved in water and decomposed with acetic acid, which precipitates the benzoylacetone in the form of small prisms.[1]

This substance melts at 60°—61°, boils almost without decomposition at 260°—262° and is readily volatile with steam. It has a very pleasant, penetrating odour, is only slightly soluble in cold, more readily in hot water and is readily soluble in alcohol and caustic soda solution. It gives an intense claret-red colouration with ferric chloride and is decomposed by boiling with alkalis into acetic acid and acetophenone.

Silver benzoylacetone, $C_6H_5.CO.CHAg.CO.CH_3$, is a white, crystalline precipitate, which is formed by the addition of silver nitrate to a solution of the ketone in ammonia.

Copper benzoylacetone, $(C_{10}H_9O_2)_2Cu$, is obtained by mixing alcoholic solutions of the ketone and copper acetate; it is a pale green precipitate, which crystallizes from hot alcohol in light green needles.

Benzoylacetonamine, $C_{10}H_{10}(NH)O$, is readily formed when the ketone is added to alcoholic ammonia; it is gradually deposited in strongly lustrous, transparent, rhombic crystals, which melt at 143° and volatilize without decomposition. It dissolves without alteration in cold mineral acids, but is decomposed, if these solutions be boiled, into ammonia and benzoylacetone.

Benzoylacetoxime, $C_{10}H_{10}(NOH)O$, is obtained by heating an alcoholic solution of benzoylacetone with an excess of hydroxylamine hydrochloride for 3—4 hours. It separates out on the addition of water and crystallizes from alcohol in lustrous scales, which melt at 65·5°—66°, have a characteristic, not unpleasant odour, a sharp taste and are volatile with steam.[2]

Isonitrosobenzoylacetone, $C_6H_5.CO.C(NOH)CO.CH_3$, is formed when a molecule of the ketone is added to an alcoholic solution of one atom of sodium, and nitrogen trioxide passed into the well-cooled solution until it has a neutral reaction. A mixture of the ketone with benzoic acid is precipitated by the addition of water, the latter being removed by means of dilute caustic soda. The isonitrosobenzoylacetone is then recrystallized from hot water, from which it separates in long, pure white needles, which melt at 123·5°—124° and form a yellow solution in alkalis (Ceresole).

Benzoylpyroracemic acid, $C_6H_5.CO.CH_2.CO.CO_2H$. When an alcoholic solution of sodium is well cooled with ice and treated

[1] Claisen and Beyer, *Ber. Deutsch. Chem. Ges.* xx. 2078.
[2] Ceresole, *ibid.* xvii. 812.

with acetophenone and ethyl oxalate in the proportions required by the following equation, the sodium compound of the ethyl ether of this acid is formed:

$$C_6H_5.CO.CH_3 + C_2H_5O.CO.CO.OC_2H_5 + C_2H_5.ONa = C_6H_5.CO.CHNa.CO.CO.OC_2H_5 + 2C_2H_5.OH.$$

If more sodium ethylate than this be employed, however, a crystalline precipitate is formed, which yields benzoylpyroracemic acid on decomposition with hydrochloric acid. This acid crystallizes from benzene in yellowish white prisms, which melt at 155°—156° and decompose at a slightly higher temperature with evolution of carbon dioxide.

Ethyl benzoyl-pyroracemate, $C_6H_5.CO.CH_2.CO.CO_2.C_2H_5$. When the sodium compound mentioned above is dissolved in ice-water and a current of carbon dioxide passed through the solution, the ether is precipitated. It crystallizes from petroleum-spirit in splendid prisms, which melt at 43°. Its alcoholic solution gives a blood-red colouration with ferric chloride and with copper acetate a precipitate of the copper compound, $(C_{12}H_{11}O_4)_2Cu$, which crystallizes from hot alcohol in fine, light green needles. The ether is decomposed into acetophenone, alcohol and oxalic acid by hot, dilute caustic soda; alcoholic ammonia acts in a similar manner, oxamide being in this case the product.[1]

DIBASIC ACIDS, $C_6H_5.C_2H_3(CO_2H)_2$.

2460 *Phenylsuccinic acid*, $C_6H_5.CH(CO_2H)CH_2.CO_2H$, was first obtained by Rügheimer, who prepared the nitril, $C_6H_5.CH(CN)CH_2.CN$, by heating β-phenylchlorethylene, $C_6H_5.CCl=CH_2$, to 200°—220° with potassium cyanide, and decomposing it by boiling with baryta water. He then obtained it in larger quantity by the action of ethyl phenylbromacetate on sodacetoacetic ether and subsequent hydrolysis of the phenylacetosuccinic ether with potash:[2]

$$\begin{array}{l} CH_3.CO.CH.CO_2.C_2H_5 \\ \qquad\quad | \\ \quad C_6H_5.CH.CO_2.C_2H_5 \end{array} + 3KOH =$$

$$\begin{array}{l} CH_2.CO_2K \\ \quad | \\ C_6H_5.CH.CO_2K \end{array} + CH_3.CO.OK + 2HO.C_2H_5.$$

[1] Beyer and Claisen, *Ber. Deutsch. Chem. Ges.* xx. 2181.
[2] *Ber. Deutsch. Chem. Ges.* xiv. 428.

Spiegel then found that it is also formed, together with toluene, when dihydrocornicularic acid, $C_6H_5.CH(CO_2H)CH_2.CO.CH_2C_6H_5$, is fused with caustic potash, and prepared it synthetically by acting upon sodium ethyl malonate with ethyl phenylchloracetate, hydrolysing the ether and heating the phenylcarboxylsuccinic acid thus obtained:[1]

$$\begin{array}{c} CH\begin{cases} CO_2H \\ CO_2H \end{cases} \\ | \\ C_6H_5.CH—CO_2H \end{array} = \begin{array}{c} CH_2.CO_2H \\ | \\ C_6H_5.CH.CO_2H \end{array} + CO_2.$$

Phenylsuccinic acid crystallizes from hot water in stellate groups of short needles, which are readily soluble in alcohol and melt at 167°.

Calcium phenylsuccinate, $C_{10}H_8O_4Ca$, is precipitated even from a dilute solution of the ammonium salt by boiling it with calcium chloride. It is thus deposited as a crystalline powder, while it separates in the cold in crystals containing two molecules of water.

Phenylsuccinic anhydride, $C_6H_5C_2H_3(CO)_2O$, is formed by heating the acid alone or with acetic anhydride and solidifies on cooling to a tough, crystalline mass, which melts between 45°—50°.

Phenylisosuccinic acid, $C_6H_5.CH_2.CH(CO_2H)_2$. The ethyl ether of this acid, which is also known as *benzylmalonic acid*, is obtained by the action of benzyl chloride on sodium ethyl malonate, as a faintly aromatic smelling liquid, which boils at 300°. The free acid is readily soluble in water and alcohol and forms asymmetric crystals, which have an aromatic odour, melt at 117° and decompose into carbon dioxide and hydrocinnanic acid when more strongly heated.[2]

Benzyltartronic acid, $C_6H_5.CH_2.C(OH)(CO_2H)_2$. The ether of benzylchloromalonic acid is formed by the action of benzylchloride on sodium chloromalonic ether and is converted by caustic potash into benzyltartronic acid. This substance is readily soluble in water and alcohol and crystallizes in lustrous prisms, which melt at 143° and decompose on further heating into carbon dioxide and α-phenyl-lactic acid.[3]

[1] *Ber. Deutsch. Chem. Ges.* xiv. 873; *Ann. Chem. Pharm.* ccxix. 29.
[2] Conrad, *ibid.* cciv. 174.
[3] *Ibid.* ccix. 243.

Cinnamic acid is always formed in addition to the benzyltartronic acid by the action of potash or baryta:[1]

$$C_6H_5.CH_2.CCl(CO_2H)_2 = C_6H_5.CH{=}CH.CO_2H + CO_2 + HCl.$$

Benzoylcyanacetic acid, $C_6H_5.CO.CH(CN)CO_2H$. The ethyl ether of this acid is formed when a mixture of ethyl benzoylacetate and an alcoholic solution of sodium ethylate is saturated with cyanogen chloride. It is readily soluble in alcohol and alkalis and forms crystals, melting at 37·5°. On boiling with water, it decomposes with formation of cyanacetophenone.[2]

PHENYLBUTYLENES OR BUTENYLBENZENES.

2461 These bodies have not yet been fully investigated.

Phenyl-α-butylene, $C_6H_5.CH{=}CH.CH_2.CH_3$, was prepared by Perkin from hydrocinnamenylacrylic acid, $C_6H_5.CH{=}CH.CH_2.CH_2.CO_2H$, by elimination of carbon dioxide. It is a liquid, which has a similar smell to styrolene, boils at 186°—187° and forms a dibromide, which crystallizes from alcohol in needles, melting at 67°.[3] This hydrocarbon is undoubtedly identical with that which Radziszewski obtained by treating boiling butylbenzene with bromine and submitting the product to distillation.[4]

Para-α-butenylphenyl methyl ether, $C_6H_4(OCH_3)C_4H_7$, is formed when methylparahydroxyphenylangelic acid is distilled and is a well-crystallized substance, which has an odour resembling that of anethol (p. 196), melts at 17° and boils at 242°—245°.[5]

Phenyl-β-butylene, $C_6H_5.CH_2.CH{=}CH.CH_3$, was obtained by Aronheim by the action of sodium on a mixture of benzyl chloride and allyl iodide, an intermolecular change taking place just as in the formation of β-butylene from methyl iodide and allyl iodide (Pt. III. p. 164).[6] It is also a product of the dry distillation of phenylhomoparaconic acid,[7] $C_{12}H_{14}O_4$, and is a liquid, boiling at 176°—177°. It forms a liquid dibromide, which decom-

[1] *Ann. Chem. Pharm.* ccix. 241.
[2] Haller, *Compt. Rend.* ci. 1270.
[3] *Journ. Chem. Soc.* 1877, ii. 667.
[4] *Ber. Deutsch. Chem. Ges.* ix. 260.
[5] Perkin, *Journ. Chem. Soc.* 1877, ii. 661.
[6] *Ann. Chem. Pharm.* clxxi. 225.
[7] Penfield, *ibid.* ccxvi. 124.

poses on heating and yields naphthalene, $C_{10}H_8$, the formation of which can readily be understood, when passed over heated lime (Pt. III. p. 38).

Phenylisobutylene, $C_6H_5.CH{=}C(CH_3)_2$, was prepared by Perkin from benzaldehyde, sodium isobutyrate and isobutyric anhydride.[1] Phenylhydroxypivalic acid, $C_6H_5.CH(OH)C(CH_3)_2CO_2H$, is the first product and then decomposes into water, carbon dioxide and phenylisobutylene.[2] This hydrocarbon is a liquid, boiling at 184°—186°, which is oxidized by chromic acid to benzoic and acetic acids. It forms a liquid dibromide, which is converted by alcoholic potash into *phenylbromisobutylene*, $C_6H_5.CBr{=}C(CH_3)_2$.

This liquid combines with bromine to form *phenylbromisobutylene dibromide*, $C_6H_5.CBr_2.CBr(CH_3)_2$, which crystallizes from acetic acid in plates, which resemble those of sublimed benzoic acid and melt at 63·5°.

Ortho-isobutenylphenol, $C_6H_4(OH)C_4H_7$, is formed when salicylaldehyde is heated with isobutyric anhydride and sodium isobutyrate:

$$C_6H_4\begin{<}{CHO}{OH} + O\begin{<}{CO.CH(CH_3)_2}{CO.CH(CH_3)_2} =$$

$$C_6H_4\begin{<}{CH{=}C(CH_3)_2}{OH} + CO_2 + HO.CO.CH(CH_3)_2.$$

The product consists of the isobutyric ether of the phenol, which is readily hydrolysed. Ortho-isobutenylphenol is a colourless liquid, which smells simultaneously of smoke and cedar wood and boils at 223°—225°.

Para-isobutenylphenol, which has been prepared from parahydroxybenzaldehyde, boils at 230° — 235° and solidifies to crystals in a freezing mixture. Its methyl ether is formed in a similar manner from anisaldehyde. It smells like anethol, boils at 236°—237° and solidifies in the cold to crystals, melting at 9°.[3]

Phenylbutylene alcohol, $C_6H_5.CH(OH)CH_2.CH_2.CH_2.OH$, is formed by the action of sodium amalgam on a dilute alcoholic solution of benzoylpropionaldehyde and is a thick liquid, which boils at about 200° and is reconverted into the aldehyde by oxidation.[4]

[1] *Journ. Chem. Soc.* 1879, i. 141.
[2] Fittig and Jayne, *Ann. Chem. Pharm.* ccxvi. 119.
[3] Perkin, *Journ. Chem Soc.* 1879, i. 142.
[4] Burcker, *Compt. Rend.* xciv. 220.

PHENYLCROTONIC ACIDS.

2462 *Phenylmethylacrylaldehyde*, $C_6H_5.CH{=}C(CH_3)CHO$, is obtained when equal molecules of benzaldehyde and propionaldehyde are dissolved in alcohol and treated with dilute caustic soda:

$$C_6H_5.CHO + CH_2\begin{matrix}CH_3\\CHO\end{matrix} = C_6H_5.CH{=}C\begin{matrix}CH_3\\CHO\end{matrix} + H_2O.$$

It is a liquid, which smells like cinnamaldehyde, combines with acid sodium sulphite and phenylhydrazine and is converted into the acid by boiling with silver oxide and dilute alcohol.[1]

Phenylmethylacrylic acid, $C_6H_5.CH{=}C(CH_3)CO_2H$, which was termed *phenylcrotonic acid* by Perkin, is formed when benzaldehyde is heated with propionic anhydride and sodium propionate,[2] or with acetic anhydride and sodium propionate[3] and is most simply prepared by heating benzidene chloride for 8—10 hours to 150° with an excess of sodium propionate[4] (p. 212).

It is also obtained, together with the benzyl ether of phenylisobutyric acid, toluene and propionic acid, by the action of sodium on benzyl propionate:[5]

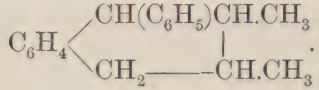
$$2\,\begin{matrix}CH_3\\|\\CH_2\\|\\CO_2.CH_2.C_6H_5\end{matrix} + 2Na = \begin{matrix}CH_3\\|\\CH_2\\|\\CO_2Na\end{matrix} + \begin{matrix}CH_3\\|\\C{=}CH.C_6H_5\\|\\CO_2Na\end{matrix} + CH_3.C_6H_5 + H_2.$$

It is slightly soluble in water, readily in alcohol, ether or benzene, and crystallizes in needles or short, oblique prisms, melting at 78°. If its solution in chloroform be treated with petroleum-spirit and a few drops of water, it separates upon evaporation of the chloroform in diamond-lustrous needles, which probably contain water (Erdmann). It is only slowly

[1] Miller and Kinkelin, *Ber. Deutsch. Chem. Ges.* xix. 525 and 1248.
[2] *Journ. Chem. Soc.* 1877, i. 391 and ii. 660; Conrad and Bischoff, *Ann. Chem. Pharm.* cciv. 188.
[3] Fittig and Slocum, *ibid.* ccxxvii. 228.
[4] Erdmann, *ibid.* ccxxvii. 247.
[5] Conrad and Hodgkinson, *ibid.* cxciii. 314; Conrad and Bischoff, *loc. cit.*

volatile with steam and boils at 288°. On heating with a mixture of four volumes of sulphuric acid and six volumes of water, it is converted into *methronene*, $C_{18}H_{20}$, an aromatic smelling liquid, which boils at 322°—323°.

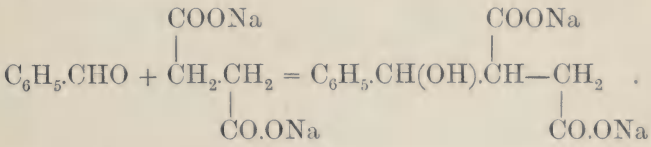
This substance, which will be subsequently described, has the following constitution :



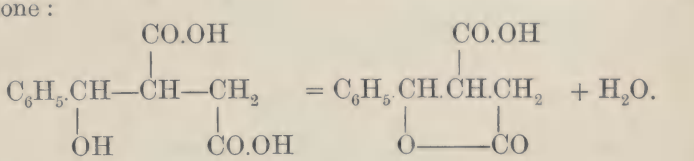
Phenylisocrotonic acid, $C_6H_5.CH{=}CH.CH_2.CO_2H$, was obtained by Perkin, who named it *isophenylcrotonic acid*, by heating benzaldehyde with succinic anhydride and sodium succinate.[1] Fittig and Jayne have found that the chief product of the reaction is phenylparaconic acid, phenylisocrotonic acid being a decomposition product of this.[2]

The reaction proceeds in the following manner :

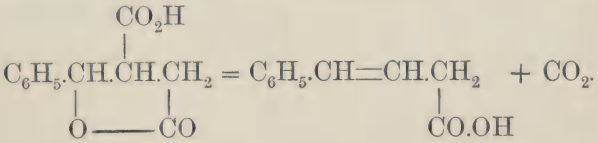
Benzaldehyde and sodium succinate combine, in a manner similar to that which occurs in the formation of aldol (Pt. II. p. 168), to form sodium phenylitamalate :



The phenylitamalic acid, however, decomposes immediately into water and phenylparaconic acid, which is simultaneously a lactone :



This is then decomposed by heating into carbon dioxide and phenylisocrotonic acid, which is, therefore, most readily prepared from phenylparaconic acid :



[1] *Journ. Chem. Soc.* 1877, i. 395. [2] *Ann. Chem. Pharm.* ccxvi. 97.

A small quantity of the isomeric phenylbutyrolactone (Pt. II. p. 168) and a little α-naphthol, $C_{10}H_7(OH)$, are simultaneously formed.[1]

Phenylisocrotonic acid is scarcely soluble in cold, only slightly in boiling water, from which it crystallizes in long, thin needles, while it separates from carbon disulphide, in which it is more readily soluble, in short, prismatic crystals. It melts at 86° and boils at 302°, almost without decomposition. On boiling with dilute sulphuric acid, it is converted into phenylbutyrolactone.[2] Other unsaturated acids are also converted into their lactones in this way, the reaction corresponding exactly to the formation of alcohols from olefines, *e.g.* that of trimethylcarbinol from isobutylene. Hydroxy-acids are first formed by the assumption of the elements of water, phenylhydroxybutyric acid being formed in the case under consideration, and then immediately decompose into the lactone and water, provided that the hydroxyl has taken the γ-position (Fittig):

$$\begin{array}{l} C_6H_5.CH{=}CH.CH_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CO.OH \end{array} + H_2O = \begin{array}{l} C_6H_5.CH.CH_2.CH_2 \\ \qquad\quad | \qquad\quad | \\ \qquad\quad OH \qquad CO.OH \end{array} =$$

$$\begin{array}{l} C_6H_5.CH.CH_2.CH_2 \\ \qquad\quad | \qquad\quad | \\ \qquad\quad O\text{———}CO \end{array} + H_2O.$$

Phenyl-a-crotonic acid or *Methylatropic acid* is formed when sodium phenylacetate is heated with paraldehyde and acetic anhydride:

$$C_6H_5.CH_2.CO_2H + COH.CH_3 = C_6H_5.C\begin{array}{l} \diagup\!\!\!\diagup CH.CH_3 \\ \diagdown CO_2H \end{array} + H_2O.$$

It crystallizes from hot water in small prisms, melting at 135°.[3]

Phenyl-a-hydroxyisocrotonic acid, $C_6H_5.CH{=}CH.CH(OH)CO_2H$. The nitril of this acid is obtained when cinnamaldehyde is dissolved in a little ether, rather more than the equivalent amount of potassium cyanide added, and concentrated hydrochloric acid then gradually run into the cooled liquid;[4] it is also formed when a mixture of oil of cinnamon and anhydrous

[1] Fittig and Erdmann, *Ann. Chem. Pharm.* ccxxvii. 242.
[2] Erdmann, *ibid.* ccxxvii. 257.
[3] Ogliarolo, *Gaz. Chim. Ital.* xv. 514.
[4] Matsmoto, *Ber. Deutsch. Chem. Ges.* viii. 1145; Peine, *ibid.* xvii. 2113.

hydrocyanic acid is allowed to stand.[1] It forms white, granular crystals, melts at 80°—81° and is converted by boiling with dilute hydrochloric acid into the acid, which crystallizes from hot water in long, flat needles, melting at 115°—116°.

HXDROXYPHENYLCROTONIC ACIDS.

2463 *Propioncoumarin*, $C_6H_4\left\langle\begin{matrix}O\text{——}CO\\ CH{=}CH\end{matrix}\right\rangle CH_3$ is prepared by heating sodium salicylaldehyde with propionic anhydride and forms rhombic crystals, which smell like coumarin and melt at 90°. It boils at 292·5° and yields salicylic acid on fusion with potash, propioncoumaric acid being first formed. Its derivatives resemble those of coumarin and, like this, it yields two series of substituted propioncoumaric acids.

α-Methylpropioncoumaric acid, $C_6H_4(OCH_3)C_3H_4.CO_2H$, forms monosymmetric crystals, melting at 118°, which are reconverted into propioncoumarin by sulphuric acid.

β-Methylpropioncoumaric acid also crystallizes in the monosymmetric system, melts at 107° and is converted by sulphuric acid into a thick, oily liquid.[2]

Methylpropionparacoumaric acid was obtained by Perkin, who heated anisaldehyde with sodium propionate and propionic anhydride. It crystallizes from alcohol in rectangular tablets, which melt at 154° and decompose into carbon dioxide and anethol when more strongly heated.[3]

β-Methylcoumarin, $C_{10}H_8O_2$, is formed by the action of concentrated sulphuric acid on a mixture of phenol and aceto-acetic ether:

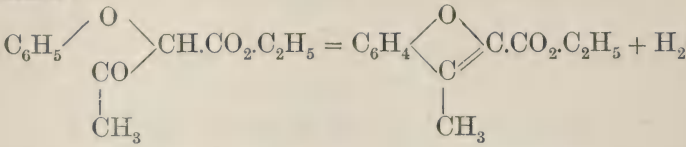
$$C_6H_4\left\langle\begin{matrix}OH\\ H\end{matrix}\right. + \begin{matrix}CO.OC_2H_5\\ |\\ CO\text{—}CH_2\\ |\\ CH_3\end{matrix} =$$

$$C_6H_4\left\langle\begin{matrix}O\text{—}CO\\ |\\ C{=}CH\\ |\\ CH_3\end{matrix}\right. + H_2O + HO.C_2H_5.$$

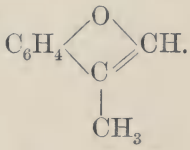
[1] Pinner, *Ber. Deutsch. Chem. Ges.* xvii. 2010.
[2] Perkin, *Journ. Chem. Soc.* 1875, x. ; 1881, i. 409.
[3] *Ibid.* 1877, i. 411.

This substance is very similar to coumarin and crystallizes from benzene in needles which melt at 125°—126°.[1]

Methylcoumarilic acid, $C_6H_4.C_2O(CH_3)CO_2H$. When phenoxylacetoacetic ether, obtained by the action of sodium phenate on chloracetoacetic ether, is treated with concentrated sulphuric acid, the ethyl ether of methylcoumarilic acid is formed :



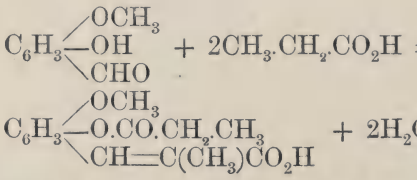
This body crystallizes from benzene in large, rhombic tablets, melts at 51°, boils at 290° and is readily saponified by alkalis. The free acid crystallizes from alcohol on gradual evaporation in small, lustrous prisms, which sublime when carefully heated, but melt at 188°—189° when rapidly heated and simultaneously decompose into carbon dioxide and methylcoumar on (p. 247), which has the following constitution :



This boils at the melting point of the acid and is a liquid which possesses an odour similar to that of naphthalene but more agreeable.[2]

DIHYDROXYPHENYLCROTONIC ACIDS.

2464 *Homoferulic acid*, $C_6H_3(OH)(OCH_3)CH{=}C(CH_3)CO_2H$. Propionhomoferulic acid is formed when vanillin is heated with sodium propionate and propionic anhydride :



[1] Pechmann and Duisberg, *Ber. Deutsch. Chem. Ges.* xvi. 2127.
[2] Hantzsch, *ibid.* xix. 1290.

It crystallizes from alcohol in needles, which melt at 128°—129°, and is converted by boiling with dilute caustic soda into homoferulic acid, which crystallizes from boiling water in flat needles, melts at 167°—168° and is resolved into iso-eugenol (p. 199) and carbon dioxide by heating with lime. It is converted by the action of sodium amalgam and water into *hydrohomoferulic acid*, which separates from hot water in crystals, melting at 114°—115°.

Methylhomoferulic acid or *Dimethylhomocaffeïc acid*, $C_6H_3(OCH_3)_2CH{=}C(CH_3)CO_2H$, is obtained by the methylation of homoferulic acid and crystallizes in pointed needles, which melt at 140°—141°.[1]

β-Methylumbelliferon, $HO.C_6H_3\begin{cases} O\text{———}CO \\ \qquad\qquad\quad | \\ C(CH_3):CH \end{cases}$, is formed when a mixture of equal molecules of resorcinol and aceto-acetic ether is brought into five times the amount of concentrated sulphuric acid. It crystallizes from hot water in lustrous needles and from alcohol in aggregates of prisms, which melt at 185° and sublime in small plates, when carefully heated. It forms a yellow solution in dilute alkalis, which shows a blue fluorescence, and this fluorescence is also shown by its colourless solution in sulphuric acid. Small quantities of resorcinol can therefore be detected by adding a little aceto-acetic ether and cold sulphuric acid.

On fusion with potash, resacetophenone $C_6H_3(OH)_2CO.CH_3$, (p. 60) is formed.[2]

Nitro-β-methylumbelliferon, $C_{10}H_7(NO_2)O_3$, is obtained by gradually adding the calculated quantity of concentrated nitric acid to glacial acetic acid containing finely divided β-methylumbelliferon in suspension. It crystallizes from boiling glacial acetic acid in straw-yellow needles.

Amido-β-methylumbelliferon, $C_{10}H_7(NH_2)O_3$, is formed by the reduction of the nitro-compound with tin and hydrochloric acid and crystallizes from hot water in yellowish needles, which melt at 247° and form a yellow solution in alkalis. The solution in concentrated sulphuric acid has a blue fluorescence, and its alcoholic solution gives an intense green colouration with ferric chloride. If it be dissolved in dilute sulphuric acid and treated with sodium nitrite, *nitroso-amido-β-methylumbelliferon*, $C_{10}H_6$

[1] Kraaz and Tiemann, *Ber. Deutsch. Chem. Ges.* xv. 2059, 2070.
[2] Pechmann and Duisberg, xvi. 2119.

$(NO)(NH_2)O_3$, is formed. This body crystallizes in yellowish red needles, forms a deep red solution in alkalis and gives Liebermann's reaction.[1]

β-Methylumbellic acid, $(HO)_2C_6H_3.C(CH_3)=CH.CO_2H$. When the calculated quantities of sodium and methylumbelliferon are dissolved in methyl alcohol and the solution heated with methyl iodide, the methyl ether of β-methylumbelliferon is formed. This is a crystalline substance, which melts at 159° and forms a solution in sulphuric acid, which shows a deep blue fluorescence. On boiling with caustic potash solution of 50 per cent., it is converted into *methyl-β-methylumbellic acid*, $(CH_3O)(OH)C_6H_3.C(CH_3)=CH.CO_2H$, which is insoluble in water and crystallizes from methyl alcohol in strongly refractive, four-sided tablets, which melt at 140° with evolution of carbon dioxide. On boiling with dilute acids it is reconverted into β-methylumbelliferon and this change is also brought about by heating with dilute ammonia (Pechmann and Duisberg). It decomposes on distillation into carbon dioxide and allylresorcinol methyl ether (Pechmann and Cohen).

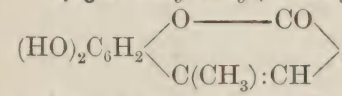
Dimethyl-β-methylumbellic acid, $(CH_3O)_2C_6H_3C(CH_3)=CH.CO_2H$. The methyl ether of this acid is obtained by heating a solution of sodium and the monomethyl-compound in wood-spirit with methyl iodide. It is an oily liquid boiling at 310°—320°. The free acid crystallizes from dilute alcohol in small needles, which melt at 145°. It is oxidized by potassium permanganate to dimethyl-β-resorcylic acid (Pechmann and Cohen).

Metahydroxymethylcoumarilic acid, $2C_6H_3(OH)C_2O(CH_3)CO_2H + H_2O$. The ethyl ether of this substance is formed when resorcinol and chloracetoacetic ether are boiled with an alcoholic solution of sodium. It crystallizes in needles which form blue fluorescent solutions in ether and the alkalis. This fluorescence disappears when the alkaline solution is boiled, the acid being formed. The latter crystallizes from hot water in needles, which become anhydrous at 110°, melt at 226° with evolution of carbon dioxide and decompose when more rapidly heated into carbon dioxide and hydroxymethylcoumaron, which slightly resembles naphthol in odour and crystallizes from hot water in needles, which melt at 96°—97° and become coloured green in the air.

All these compounds give violet colourations on heating with sulphuric acid.[2]

[1] Pechmann and Cohen, *Ber. Deutsch. Chem. Ges.* xvii. 2129.
[2] Hantzsch, *ibid.* xix. 2927.

TRIHYDROXYPHENYLCROTONIC ACIDS.

2465 *v-Dihydroxy-β-methylcoumarin* or *β-Methyldaphnetin*,  , has been prepared from pyrogallol and aceto-acetic ether and crystallizes from hot water in needles, which melt at 235°. Its solution in dilute alcohol gives an intense green colouration with ferric chloride. It forms a yellow non-fluorescent solution in alkalis and its solution in sulphuric acid is also non-fluorescent.[1] If it be boiled with sodium bisulphite solution until complete solution has taken place and be then treated with ferric chloride, the liquid is coloured deep blue, while ammonia and potassium ferricyanide produce a reddish yellow colouration[2] (p. 255).

a-*Dihydroxy-β-methylcoumarin* has been prepared from phloroglucinol and crystallizes from alcohol in needles, which melt at 282°—284°. The alkaline solution is also non-fluorescent and the compound is therefore probably not the true homologue of aesculetin (p. 256) (Pechmann and Cohen).

Dihydroxymethylcumarilic acid, $2C_6H_2(OH)_2C_2O(CH_3)CO_2H + H_2O$, has also been prepared from phloroglucinol. It forms crystals, which become anhydrous at 120° and melt at 281° with decomposition. When it or its ether is heated with concentrated sulphuric acid, an indigo-blue solution is obtained.[3]

Scopoletin, $C_{10}H_8O_4$, is a constituent of the root of *Scopolia japonia*, the Japanese Belladonna,[4] and is, according to Paschkis,[5] identical with the "Schillerstoff" of the deadly nightshade (*Atropa Belladonna*), which was termed chrysatropic acid by Kunz.[6]

Scopoletin crystallizes from alcohol in needles, which are only slightly soluble in cold, rather more readily in hot water, melt at 198° and sublime when more strongly heated. Its solution has a faint acid reaction and shows a blue fluorescence.

[1] Pechmann and Duisberg, *Ber. Deutsch. Chem. Ges.* xvi. 2127.
[2] Pechmann and Cohen, *ibid.* xvii. 2189.
[3] Lang, *ibid.* xix. 2934.
[4] Eijkman, *ibid.* xvii. Ref. 442.
[5] *Ibid.* xix. Ref. 305.
[6] *Ibid.* xix. Ref. 104.

Scopolin, $C_{24}H_{30}O_{15}+2H_2O$, occurs together with scopoletin and crystallizes in needles, which melt at 218°. On continued boiling with dilute sulphuric acid it decomposes into scopoletin and glucose:

$$C_{24}H_{30}O_{15} + 2H_2O = C_{12}H_{10}O_5 + 2C_6H_{12}O_6.$$

The root also contains scopoleïn, a poisonous substance, which is closely related to atropine.

KETONES $C_{10}H_{10}O$

2466 *Benzalacetone* or *Acetocinnamone*, $C_6H_5.C_2H_2.CO.CH_3$, is formed in small amount, together with other products by the distillation of a mixture of calcium acetate and calcium cinnamate [1] and is also formed when benzaldehyde and acetone are heated with acetic anhydride and zinc chloride for some time.[2] It may however be much more conveniently prepared by the action of very dilute caustic soda on an aqueous solution of benzaldehyde and acetone: [3]

$$C_6H_5.CHO + CH_3.CO.CH_3 = C_6H_5.CH{=}CH.CO.CH_3 + H_2O.$$

It crystallizes in lustrous, thick, quadratic tablets, melts at 41°—42°, boils at 260°—262° and possesses an odour which resembles those of coumarin and rhubarb. Applied to sensitive portions of the skin, it produces an unpleasant burning and itching sensation. It combines with bromine to form *methyldibromostyrolylketone*, $C_6H_5.CHBr.CHBr.CO.CH_3$, which crystallizes from alcohol in short needles, and melts at 124°—125° with decomposition.

KETONES, $C_{10}H_{10}O_2$.

2467 *Methylcoumarylketone*, $C_6H_4(OH)CH{=}CHCO.CH_3$. When an aqueous solution of helicin (Pt. IV. p. 288) is heated with acetone and dilute caustic soda solution, *glucomethylcoumarylketone*, $C_6H_4(O.C_6H_{11}O_5)C_2H_2.CO.CH_3$, is formed. This crystallizes

[1] Engler and Leist, *Ber. Deutsch. Chem. Ges.* vi. 254.
[2] Claisen and Claparède, *ibid.* xiv. 2461.
[3] Claisen and Ponder, *Ann. Chem. Pharm.* ccxxiii. 137.

from hot water in yellowish needles, which melt at 192° and are converted by emulsin into methylcoumarylketone, which crystallizes from alcohol in long, white needles, melting at 139°.[1]

Methylferuloketone, $C_6H_3(OH)(OCH_3)CH{=}CH.CO.CH_3$. The glucoside of this compound is obtained by the action of dilute caustic soda solution on glucovanillin and acetone, and crystallizes from boiling water in light yellow needles, which contain two molecules of water and melt at 207°. The free methylferuloketone, which is prepared from this by means of emulsin, crystallizes in light yellow needles, which melt at 130° and dissolve readily in alcohol but only slightly in water.[2]

KETONIC ACIDS, $C_{10}H_8O_3$.

2468 *Cinnamylformic acid*, $C_6H_5.CH{=}CH.CO.CO_2H$. was first obtained from its nitril, but is more readily prepared by the action of hydrochloric acid on a mixture of benzaldehyde and pyroracemic acid :[3]

$$C_6H_5.CHO + CH_3.CO.CO_2H = C_6H_5.CH{=}CH.CO.CO_2H + H_2O.$$

It forms a syrup which dries to a gummy mass and is readily decomposed by alkalis into pyroracemic acid and benzaldehyde.

Cinnamylformonitril, $C_6H_5.CH{=}CH.CO.CN$, is obtained by heating cinnamyl chloride with silver cyanide, and crystallizes from ether in prisms or tablets, melts at 114°—115° and is converted by the addition of concentrated hydrochloric acid to its solution in acetic acid into *cinnamylformamide*, $C_6H_5.C_2H_2.CO.CO.NH_2$, which crystallizes from hot water in small plates or prisms, melting at 129°—130°.[4]

Benzoylacrylic acid, $C_6H_5.CO.CH{=}CH.CO_2H$, is formed by the action of aluminium chloride on a mixture of benzene and maleïc anhydride, and crystallizes from hot water in lustrous satiny plates, which contain water, while it separates from toluene in needles, melting at 99°. On heating with alkalis it is resolved into acetophenone and glyoxylic acid, which is then

[1] Tiemann and Kees, *Ber. Deutsch. Chem. Ges.* xviii. 1955.
[2] Tiemann, *ibid.* xviii. 3492.
[3] Claisen and Claparède, *ibid.* xiv. 2472.
[4] Claisen and Antweiler, *ibid.* xiii. 2123.

further converted into glycolic and oxalic acids. It yields benzoylpropionic acid and other products on reduction. When it is heated with acetic anhydride to 150°—160° in a sealed tube, lustrous, ruby-red needles or plates of a compound $C_{10}H_6O_2$ separate out, which sublime on heating and dissolve in a mixture of benzene and petroleum spirit to form a rose-red solution with a golden-yellow fluoresence. It slowly dissolves in sulphuric acid to form a bright blue solution and is reprecipitated by the addition of water. If the solution be heated, the colour changes to red, and a deep green fluorescence is then produced by the addition of water. Reducing agents convert the red compound, which is probably a quinone, into a colourless, crystalline substance.[1]

DIBASIC ACIDS, $C_{10}H_8O_4$.

2469 *Benzalmalonic acid*, $C_6H_5.C_2H(CO_2H)_2$, is formed when a mixture of equal parts of benzaldehyde and malonic acid is heated with half its weight of glacial acetic acid for some hours on the water-bath; the following reaction taking place:[2]

$$C_6H_5.CHO + CH_2(CO_2H)_2 = C_6H_5.CH(OH)CH(CO_2H)_2$$
$$= C_6H_5.CH{=}C(CO_2H)_2 + H_2O.$$

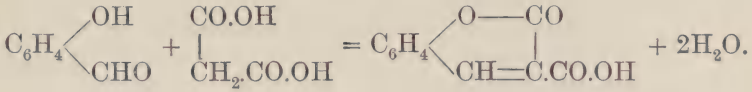
It crystallizes from hot water in thick, vitreous prisms, which decompose on heating into carbon dioxide and cinnamic acid. The latter is also formed when the acid is boiled with water, but the chief products of this decomposition are benzaldehyde and malonic acid. It is converted into benzylmalonic acid by sodium amalgam and water.

Ethyl benzalmalonate, $C_6H_5.C_2H(CO_2.C_2H_5)_2$, is readily obtained by passing hydrochloric acid into a mixture of ethyl malonate and benzaldehyde, and is a thick, almost odourless liquid, which boils at 196°—200° at a pressure of 13—14 mm. Small quantities can be rapidly distilled at the ordinary pressure, the boiling-point being 308°—312°.

The three nitrobenzalmalonic acids have been prepared from the corresponding nitrobenzaldehydes.[3]

[1] Pechmann, *Ber. Deutsch. Chem. Ges.* xv. 881.
[2] Claisen and Crismer, *Ann. Chem. Pharm.* ccxviii. 129.
[3] Stuart, *Journ. Chem. Soc.* 1883, i. 403; 1885, i. 155; 1886, i. 357.

Coumarincarboxylic acid, $C_{10}H_6O_4$, is the lactone of the unknown hydroxybenzalmalonic acid, and is formed by heating salicylaldehyde with malonic acid and glacial acetic acid to 100°:



It crystallizes from hot water in white needles, which melt at 187° and decompose into coumarin and carbon dioxide when more strongly heated.[1]

HYDROCARBONS OF THE FORMULA, $C_6H_5.C_4H_5$.

2470 *Ethylphenylacetylene*, $C_6H_5.C{\equiv}C.C_2H_5$, is formed when a mixture of sodium phenylacetylene, ethyl iodide and ether is heated to 140°. It is a strongly refractive liquid, which has a characteristic odour, boils at 201°—203° and has a sp. gr. of 0·923 at 21°. It combines at 150° with fuming hydrobromic acid to form *ethylphenylvinyl bromide*, $C_6H_5.C_2HBr.C_2H_5$, a liquid, which smells like peppermint, decomposes on distillation and is converted into *ethylphenylvinyl acetate*, $C_6H_5.C_2H(OC_2H_3O)C_2H_5$, by heating with silver acetate and glacial acetic acid.

This substance has a pleasant odour, boils at 223°—230° and on saponification yields *ethylphenylvinyl alcohol*, $C_6H_5.C_2H(OH)C_2H_5$, which is also a pleasant-smelling liquid and boils at 224°—226°. Its constitution is represented by one of the following formulæ :[2]

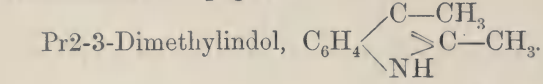
$$C_6H_5.CH{=}C(OH)C_2H_5 \qquad C_6H_5.C(OH){=}CH.C_2H_5.$$

Phenylcrotonylene, $C_6H_5.CH_2.C{\equiv}C.CH_3$, was obtained by Aronheim by heating phenyl-β-butylene dibromide (p. 326) with alcoholic potash. It is a liquid, which boils at 185°—190° and does not give a silver compound.

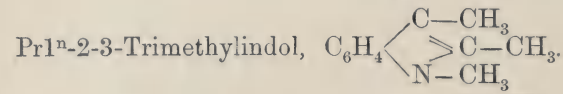
[1] Stuart, *Journ. Chem. Soc.* 1886, i. 365.
[2] Morgan, *ibid.* 1876, i. 162.

INDOLS, $C_{10}H_{11}N$.

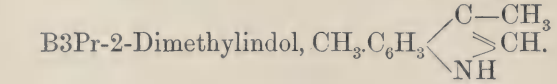
2471 The following have been investigated:[1] for explanation of the nomenclature see page 269:

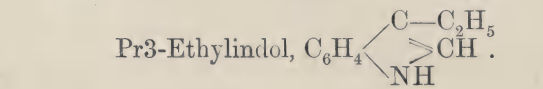


Pr2-3-Dimethylindol, $C_6H_4\left\langle\begin{matrix}C-CH_3\\ \geqslant C-CH_3.\\ NH\end{matrix}\right.$



Pr1^n-2-3-Trimethylindol, $C_6H_4\left\langle\begin{matrix}C-CH_3\\ \geqslant C-CH_3.\\ N-CH_3\end{matrix}\right.$





B3Pr-2-Dimethylindol, $CH_3.C_6H_3\left\langle\begin{matrix}C-CH_3\\ \geqslant CH.\\ NH\end{matrix}\right.$

Pr3-Ethylindol, $C_6H_4\left\langle\begin{matrix}C-C_2H_5\\ \geqslant CH\ .\\ NH\end{matrix}\right.$

*Pr*2-3-*Dimethylindol* is formed when methylindolacetic acid, which is the corresponding carboxylic acid, is heated and when the phenylhydrazone of methylethylketone is heated to 180° with zinc chloride. It crystallizes in small plates, smells like indol, melts at 106°, boils at 285° and does not colour a pine-splinter which has been moistened with hydrochloric acid. Its picrate forms red needles.

Trimethylindol is obtained by heating dimethylindolacetic acid and is an oily liquid, which boils at about 280°, has only a faint odour, does not colour pine-wood and also forms a picrate, which crystallizes in dark red needles.

*B*3-*Pr*2-*Dimethylindol* is prepared in a similar manner to methylketol from acetoneparatolylhydrazone; it forms crystals, which melt at 114°—115° and yields a picrate crystallizing in dark red needles and melting at 155°.

*Pr*3-*Ethylindol* is obtained by heating lactic acid with aniline and zinc chloride. It is a light yellow liquid, which has a fæcal odour, boils at 282°—284° and gives the pyrrol reaction. The addition of bromine to its solution in chloroform produces a deeply-coloured solution resembling one of potassium permanganate. Its picrate is readily soluble in benzene and is precipitated from this solution in red flakes, which melt at 143°.[2]

[1] Fischer, *Ann. Chem. Pharm.* ccxxxvi. 216; Degen, *ibid.* ccxxxvi. 151; Raschen, *ibid.* ccxxxix. 223.

[2] Pictet and Duparc, *Ber. Deutsch. Chem. Ges.* xx. 3415.

INDOLCARBOXYLIC ACIDS CONTAINING TEN CARBON ATOMS.

The following members of this group are known:

Skatolcarboxylic acid, $C_6H_4\left\langle\begin{matrix}C-CH_3\\ \\ NH\end{matrix}\right\rangle C-CO_2H.$

Pr1^n-2-3-Dimethylindolcarboxylic acid, $C_6H_4\left\langle\begin{matrix}C-CO_2H\\ \\ NCH_3\end{matrix}\right\rangle C-CH_3.$

Indoldicarboxylic acid, $C_6H_4\left\langle\begin{matrix}CH\\ NH\\ CO_2H\end{matrix}\right\rangle C-CO_2H.$

B3-Pr2-Methylindolcarboxylic acid
B1-Pr2-Methylindolcarboxylic acid $\Big\}$ $CH_3.C_6H_3\left\langle\begin{matrix}CH\\ NH\end{matrix}\right\rangle C-CO_2H$

Skatolcarboxylic acid is an invariable product of the putrefaction of egg-albumen[1] and appears to be a normal constituent of human urine.[2] It crystallizes from benzene in odourless plates, which melt at 164° and decompose at a higher temperature into skatol and carbon dioxide. The dilute, 0·1 per cent. solution is coloured cherry-red by the addition of a few drops of pure nitric acid followed by a small quantity of potassium nitrite solution, and a red colouring-matter separates out on standing, while a purple-red colouring-matter is produced when the solution is mixed with an equal volume of hydrochloric acid of sp. gr. 1·2 and heated with a few drops of bleaching powder solution. When ferric chloride is added to a solution of skatolcarboxylic acid made faintly acid with hydrochloric acid, an intense violet colouration is produced even in a solution containing only 0·001 per cent.

Pr1^n-2-3-Dimethylindolcarboxylic acid. The ethyl ether of this acid is obtained by heating the methylphenylhydrazone of aceto-acetic ether with zinc chloride and yields the free acid on treatment with alcoholic potash and decomposition of the product with dilute sulphuric acid. It crystallizes from hot alcohol in small, lustrous, six-sided tablets, which melt at 185° with partial decomposition and decompose at 200°—205° into carbon dioxide and dimethylindol (p. 269).[3]

[1] H. and E. Salkowski, *Ber. Deutsch. Chem. Ges.* xiii. 191; xviii. Ref. 410.
[2] *Ibid.* xviii. Ref. 411.
[3] Degen, *Ann. Chem. Pharm.* ccxxxvi. 157.

Indoldicarboxylic acid. When metahydrazinebenzoic acid is treated with pyroracemic acid in faintly acid solution, the corresponding hydrazone, $C_{10}H_{10}N_2O_4$, is formed and is converted into the ethyl ether by heating with sulphuric acid and alcohol. This ether, on heating to 215°—220° with zinc chloride, yields among other products the mono-ethyl ether of indoldicarboxylic acid, from which the free acid may readily be prepared. It crystallizes from hot alcohol in fine needles, melts with evolution of gas at 250°, carbonization taking place and a small quantity of distillate being obtained, which appears to contain indol.[1]

*B*3-*Pr*2-*Methylindolcarboxylic acid* has been prepared from pyroracemic acid paratolylhydrazone and crystallizes from hot water in needles, which melt at 227°—228° and decompose into carbon dioxide and B3-methylindol at 235°—240°.

*B*1-*Pr*2-*Methylindolcarboxylic acid* forms needles, which melt at 170°—171° and only yield a very small amount of B1-methylindol when more strongly heated (Raschen).

[1] Röder, *Ann. Chem. Pharm.* ccxxxvi. 167.

THE LAURENE GROUP.

THE HYDROCARBONS OF THE FORMULA, $C_{11}H_{16}$.

2472 The first member of this group to be synthetically prepared was amylbenzene, which was obtained by Fittig and Tollens. The isomeric laurene, after which the group is named, was then obtained, accompanied by other products, by the distillation of camphor with zinc chloride (Fittig, Köbrich, and Jilke).

PENTAMETHYLBENZENE, $C_6H(CH_3)_5$.

This body was discovered by Friedel and Crafts, who obtained it, together with other methylated benzenes, by the action of methyl chloride on benzene and toluene in presence of aluminium chloride.[1] As already mentioned, the latter yields orthoxylene, together with a little paraxylene and still less metaxylene. On further methylation, the dimethylbenzenes are converted into pseudocumene, metaxylene yielding some mesitylene in addition. The former of these then passes into durene and the latter into isodurene, both of which finally yield pentamethylbenzene and hexmethylbenzene, which can therefore be readily obtained directly from mesitylene.[2] The methylation of benzene can therefore be expressed by the following diagram, the chief products being italicised (Jacobsen).

Orthoxylene
Toluene—Paraxylene—*Pseudocumene - Durene*—Penta- and Hexmethylbenzene.
Metaxylene—Mesitylene - Isodurene—

[1] *Ann. Chim. Phys.* [6] i. 459 ; Ador and Rilliet, *Ber. Deutsch. Chem. Ges.* xii. 329.

[2] Jacobsen, *ibid.* xiv. 2624 ; xx. 896.

Pentamethylbenzene crystallizes in large plates, melts at 53° and boils at 229°.

Bromopentamethylbenzene, $C_6Br(CH_3)_5$, is formed by the action of bromine on the hydrocarbon in chloroform solution; the reaction is assisted by the presence of a trace of iodine. It forms white crystals, melts at 163° and boils at 292°.

Pentamethylsulphonic acid, $C_6(SO_3H)(CH_3)_5$, is not formed when the hydrocarbon is agitated with sulphuric acid, the products in this case being hexmethylbenzene and prehnitenesulphonic acid (p. 277). It may however be obtained by gradually bringing the hydrocarbon into well-cooled chlorosulphonic acid, the sulphone being also formed. The sodium salt, $C_6(SO_3Na)(CH_3)_5$, crystallizes in tabular crusts and is only slightly soluble in hot water. If it be agitated with sulphuric acid in presence of petroleum-spirit until complete solution has taken place, the latter leaves a residue of pure pentamethylbenzene on evaporation (compare p. 275).

Pentamethylbenzenesulphonic chloride, $C_6(SO_2Cl)(CH_3)_5$, crystallizes from warm alcohol in small plates and from ether in large flat prisms, melting at 82°.

Pentamethylbenzenesulphonamide, $C_6(SO_2.NH_2)(CH_3)_5$, separates from hot alcohol in large, flat, lustrous prisms, which melt at 186°.[1]

Pentamethylphenol, $C_6(OH)(CH_3)_5$, was obtained by Hofmann by suspending the sulphate of amidopentamethylbenzene in a solution of potassium nitrite and adding dilute sulphuric acid to the well-cooled mixture until complete solution had taken place. It crystallizes from alcohol in fine needles, has the characteristic smell of phenol, melts at 125°, boils at 267° and is volatile with steam. Ferric chloride produces no colouration and caustic soda only dissolves it on warming.

Pentamethylphenyl methyl ether, $C_6(OCH_3)(CH_3)_5$, crystallizes from alcohol in long needles, melting at 63°—64.°

Amidopentamethylbenzene, $C_6(NH_2)(CH_3)_5$, is formed when dimethyl-*a*-pseudocumidine is heated with methyl iodide to 240°—250°. It crystallizes from dilute alcohol in large white needles, melts at 151°—152° and boils at 277°—278°.

	Melting-point.
Methylamidopentamethylbenzene, $C_6(CH_3)_5.NH(CH_3)$	60°—61°
Dimethylamidopentamethylbenzene, $C_6(CH_3)_5N(CH_3)_2$	53°—54°
Acetamidopentamethylbenzene, $C_6(CH_3)_5NH(C_2H_3O)$	213°

[1] Jacobsen, *Ber. Deutsch. Chem. Ges.* xx. 896.

These compounds crystallize in needles; the dimethylated base does not combine with methyl iodide even at 170°.

Pentamethylphenylcarbamine, $C_6(NC)(CH_3)_5$, has been prepared by heating the amido-base with alcoholic caustic soda and chloroform, and forms colourless crystals, melting at 127°—128°, which, although exceedingly unpleasant, do not possess such an overpowering odour as the more volatile carbamines. When heated above its melting point, it changes with evolution of heat into the isomeric nitril, $C_6(CN)(CH_3)_5$, which crystallizes from alcohol in white needles, melting at 168° and boils at 290°—292°. It has been found impossible to convert this substance into the corresponding amide or acid. It is not attacked by sulphuric acid at 100° or hydrochloric acid at 180°, while at 250° it is partially carbonized. On heating to 220°—230° with concentrated hydriodic acid, it is decomposed into ammonia, carbon dioxide and pentamethylbenzene, so that in this respect it resembles the corresponding derivates of isoduridine (p. 276).

Pentamethylphenylthiocarbimide, $C_6(NCS)(CH_3)_5$, is formed, together with the corresponding thiocarbamide by the continued heating of the amido-base with carbon disulphide. The mustard oil passes over on distillation with steam. It crystallizes from alcohol in needles, melting at 86°.[1]

Tetramethylbenzenecarboxylic acid, $C_6H(CH_3)_4CO_2H$, is formed by the oxidation of pentamethylbenzene with dilute nitric acid and crystallizes from alcohol in fascicular groups of needles, which melt at 165°. On heating with caustic lime it yields prehnitene, its constitution being thus ascertained.[2]

Trimethylbenzenedicarboxylic acid, $C_6H(CH_3)_3(CO_2H)_2$, has been obtained by the oxidation of durylphenylketone, $C_6H(CH_3)_4 CO.C_6H_5$, with potassium permanganate and crystallizes from water in needles, which melt at 210°. On heating the solution of the ammonium salt with barium chloride, the compound $C_6H(CH_3)_3(CO_2)_2Ba + H_2O$ is precipitated in fine needles.[3]

Benzenepentacarboxylic acid, $C_6H(CO_2H)_5 + 6H_2O$, is formed when finely powdered pentamethylbenzene is added to a solution of potassium permanganate and the mixture allowed to stand for a month. It is left on the evaporation of its solution as an amorphous mass, which loses its water on heating, then melts

[1] Hofmann, *Ber Deutsch. Chem. Ges.* xviii. 1821.
[2] Gottschalk, *ibid.* xx. 3286.
[3] Ador and Meyer, *Jahresber. Chem.* 1879, 562.

and finally yields a crystalline sublimate, a portion being simultaneously carbonized. It forms a characteristic calcium salt, $(C_{11}HO_{10})_2Ca$, which crystallizes very slowly in spherical aggregates of small needles. The salts of most of the metals produce amorphous precipitates in a solution of the acid neutralized with sodium carbonate (Friedel and Crafts).

S-METHYLDIETHYLBENZENE, $C_6H_3(CH_3)(C_2H_5)_2$.

2473 This substance was prepared by Jacobsen, together with mesitylene, dimethylethylbenzene and a small quantity of triethylbenzene, by distilling a mixture of acetone and methylethylketone with sulphuric acid. It is also a constituent of Caucasian petroleum[1] and is a liquid boiling at 198°—200°, which has a specific gravity of 0·879 at 20°. On oxidation with nitric acid it yields uvitic acid.

Tribromomethyldiethylbenzene, $C_6Br_3(CH_3)(C_2H_5)_2$, crystallizes from hot alcohol in fine needles, melting at 206°.[2]

Diethylbenzoic acid, $C_6H_3(C_2H_5)_2CO_2H$, is formed, together with hydrogen and benzoic acid, when diethylcarbobenzonic acid, $C_{18}H_{18}O_2$, is heated with caustic potash and is an oily liquid; the silver salt crystallizes in small plates.[3]

THE DIMETHYLPROPYLBENZENES, $C_6H_3(CH_3)_2C_3H_7$.

2474 *s-Dimethylpropylbenzene* has been prepared by Jacobsen from acetone and methylpropylketone; it boils at 210° and is oxidized by nitric acid to mesitylenic acid.[4]

Laurene is formed, together with lower homologues, by the distillation of camphor with zinc chloride and boils at 188°.

Tribromolaurene, $C_6Br_3(CH_3)_2C_3H_7$, crystallizes from alcohol in long needles, melting at 125°.[5] It was supposed by Montgolfier that laurene was isomeric with cymene[6] whilst Armstrong and Miller considered it to be identical with ethylorthoxylene.[7] Reuter

[1] Markownikow, *Ann. Chem. Pharm.* ccxxxiv. 107.
[2] *Ber. Deutsch. Chem. Ges.* vii. 1430.
[3] *Ann. Chem. Pharm.* clxxxiv. 172.
[4] *Ber. Deutsch. Chem. Ges.* viii. 1259.
[5] Fittig, Köbrich, and Jilke, *Ann. Chem. Pharm.* cxlv. 129.
[6] *Ann. Chim. Phys.* [5] xiv. 91.
[7] *Ber. Deutsch. Chem. Ges.* xvi. 2255.

has however found that it is a mixture of two dimethylpropylbenzenes, which can readily be separated by means of their sulphonic acids.[1]

α-Laurene ($C_3H_7 : CH_3 : CH_3$=1 : 3 : 4) boils at 190°—191°, is oxidized to paraxylic acid by nitric acid and yields bromine derivatives, which all crystallize well.

α-Laurenesulphonic acid, $C_6H_2(C_3H_7)(CH_3)_2SO_3H$, forms well-developed, asymmetric crystals.

Sodium laurenesulphonate, $C_{11}H_{15}SO_3Na$, crystallizes in large, transparent plates.

Barium laurenesulphonate, $(C_{11}H_{15}SO_3)_2Ba + 5H_2O$, forms long, six-cornered crystals.

α-Laurenesulphonamide, $C_{11}H_{15}SO_2.NH_2$, crystallizes in long needles, which melt at 127°.

β-Laurene (1 : 2 : 4) boils at 184°—186°, and is oxidized to xylic acid by nitric acid. Its sulphonic acid is liquid and forms amorphous, readily soluble salts; the sulphonamide only becomes solid after standing for weeks.

Methylpropylbenzoic acid or *Cymenecarboxylic acid*, $C_6H_3(C_3H_7)(CH_3)CO_2H$(1 : 4 : 3). The nitril is obtained by the distillation of sodium cymenesulphonate with potassium cyanide and is converted by heating with alcoholic potash into the amide, from which the acid may be obtained by heating with hydrochloric acid. The free acid crystallizes in fine needles, melting at 63°.[2]

Propylorthotoluic acid (1 : 4 : 2). The nitril of this acid is formed when carvacryl phosphate, $[C_3H_7(CH_3)C_6H_3]_3PO_4$, is heated with potassium cyanide. It is an aromatic smelling liquid, which boils at 244°—246°. The corresponding acid crystallizes from dilute alcohol in needles, melting at 75°.[3]

Thymotic acid, $C_6H_2(OH)C_3H_7(CH_3)CO_2H$(2 : 1 : 4 : 3), is obtained by passing carbon dioxide into a mixture of thymol and sodium; it forms small, silky crystals, which are only slightly soluble even in hot water, melt at 123° (Kobek) and volatilize with steam. It gives a deep blue colouration with ferric chloride.[4]

Thymotide, $C_{11}H_{12}O_2$, corresponds to salicylide (Pt. IV. p. 308) and is formed when the acid is heated with phosphorus pentoxide or the potassium salt with phosphorus pentachloride; it crystallizes in needles and melts at 187°.[5]

[1] Reuter, *Ber. Deutsch. Chem. Ges.* xvi. 624.
[2] Paternò and Fileti, *Gaz. Chim. Ital.* v. 30.
[3] Kreysler, *Ber. Deutsch. Chem. Ges.* xviii. 1714.
[4] Kolbe and Lautemann, *Ann. Chem. Pharm.* cxv. 205.
[5] Naquet, *Bull. Soc. Chim.* iv. 92.

Parathymotic acid (2 : 1 : 4 : 5). The aldehyde of this acid is obtained by heating thymol with caustic soda and chloroform, and crystallizes from hot water, in which it is only very slightly soluble, in long, silky needles, which melt at 133°. The acid may be obtained in a similar manner by employing tetrachloromethane instead of chloroform in the reaction. It crystallizes from dilute alcohol in broad, white plates, melts at 157° and gives no reaction with ferric chloride.[1]

Carvacrotic acid (3 : 1 : 4 : 2) has been prepared by treating carvacrol with sodium and carbon dioxide, and crystallizes from hot water in long, smooth needles, which melt at 131° (Lustig) and readily sublime. It gives a bluish-violet colouration with ferric chloride.[2]

Paracarvacrotic acid (3 : 1 : 4 : 6). The aldehyde of this acid is formed when carvacrol is heated with chloroform and caustic soda, and is a heavy, oily liquid, which decomposes on distillation, but is volatile with steam. It is readily oxidized by exposure to the air, more rapidly by a cold solution of potassium permanganate.

Paracarvacrotic acid crystallizes from hot water in very fine silky needles, which melt at 80°, readily sublime and give a green colouration with ferric chloride.[3]

Cymenotic acid (4 : 1 : 3 : 5), has been prepared by the action of sodium and carbon dioxide on meta-isocymophenol (p. 302). It is only slightly soluble in hot water, from which it crystallizes in long, fine needles, melting at 147°. It gives a bluish violet colouration with ferric chloride.[4]

METHYLBUTYLBENZENES OR BUTYLTOLUENES.

2475 *Meta-isobutyltoluene*, $C_6H_4(CH_3)CH_2.CH(CH_3)_2$, was discovered by Kelbe in spirit of resin,[5] and synthetically prepared by the action of isobutylbromide on a mixture of toluene and aluminium chloride.[6] The butyltoluene, which Goldschmidt

[1] Kobek, *Ber. Deutsch. Chem. Ges.* xvi. 2096.
[2] Kekulé and Fleischer, *ibid.* vi. 1087.
[3] Lustig, *ibid.* xix. 11.
[4] Jesurun, *ibid.* xix. 1413.
[5] Kelbe, *ibid.* xiv. 1240; Renard, *Ann. Chim. Phys.* [6] i. 250.
[6] Kelbe and Baur, *ibid.* xvi. 2559.

obtained by heating isobutyl alcohol with toluene and zinc chloride to 300°, is probably identical with this substance.[1]

It is extracted from resin spirit by converting the fraction which boils at 190°—200° into the sulphonic acids and preparing the pure lead salt, which is then decomposed by heating with hydrochloric acid. It is a strongly refractive liquid, which has a pleasant odour, boils at 186°—188° and is oxidized by chromic acid to isophthalic acid.

Meta-isobutyltoluenesulphamide, $C_6H_3(SO_2.NH_2)(CH_3)C_4H_9$, crystallizes from water in small, lustrous plates, which melt at 74°—75°.

Isobutylorthocresol, $C_6H_3(OH)(CH_3)C_4H_9$, has been obtained from the following compound by means of the diazo-reaction, as a thick liquid, which has a faint aromatic odour and boils at 235°—237°.

a-Isobutylorthotoluidine, $C_6H_3(NH_2)CH_3.C_4H_9(6:1:3)$, is prepared by heating orthotoluidine hydrochloride with isobutyl alcohol to 200°—300°, and is a pleasantly aromatic smelling liquid, which boils at 243° and yields a diazo-salt, which is converted into meta-isobutyltoluene by heating with stannous chloride.[2]

v-Isobutylorthotoluidine (2 : 1 : 3), is formed when orthotoluidine is heated to 280° with isobutyl alcohol and zinc chloride,[3] and is a liquid which has a less pleasant odour than the preceding compound, boils at the same temperature and may also be converted into meta-isobutyltoluene by the diazo-reaction.

These bases can easily be separated by means of their salts and other derivatives. Their constitution follows from the facts that the first described forms a mustard oil, which on heating with copper yields the nitril of isobutylorthotoluic acid, $C_6H_3(CH_3)(C_4H_9)CO_2H$, the free acid corresponding to which is converted by oxidation into trimellitic acid, and that only two isomeric amido-bases can be formed by the reaction employed in their preparation.

Para-isobutyltoluene also occurs in essence of resin and is formed, together with the meta-compound, by the aluminium bromide synthesis.[4] It is a liquid, which has a pleasant smell and boils at 176°—178°.

[1] *Ber. Deutsch. Chem. Ges.* xv. 1066.
[2] Effront, *ibid.* xvii. 2317.
[3] Erhardt, *ibid.* xvii. 419; Effront, *loc. cit.*
[4] Kelbe and Pfeiffer, *ibid.* xix. 1723.

Para-isobutyltoluenesulphamide crystallizes in large, vitreous plates, which melt at 113°.

Meta-isobutylbenzoic acid, $(CH_3)_2C_2H_3.C_6H_4.CO_2H$, is formed by the oxidation of meta-isobutyltoluene with dilute nitric acid, the reaction being somewhat exceptional inasmuch as the more complex side chain is not attacked. It crystallizes in long broad needles, melting at 127°; on heating to 170°—200° with nitric acid, isophthalic acid is formed (Kelbe and Pfeiffer).

Para-isobutylbenzoic acid, which is formed in a similar manner from para-isobutyltoluene, was first synthetically prepared by Pahl, who converted isobutylphenyl mustard oil into *para-isobutylbenzonitril*, $C_4H_9.C_6H_4.CN$, by heating it with copper dust. The nitril is an aromatic smelling liquid, which boils at 248° and is converted into the acid by heating with alcoholic potash.[1] The free acid is also formed when isobutylformanilide, $C_4H_9.C_6H_4N(COH)H$, is heated with zinc dust,[2] and when isobutylphenyl phosphate is heated with potassium cyanide.[3] Para-isobutylbenzoic acid forms needles or monosymmetric crystals, which resemble those of calc spar in shape and melt at 164°. It is oxidized to terephthalic acid by potassium permanganate or by nitric acid at 170°—200°.

Both these acids are resolved into carbon dioxide and isobutylbenzene by heating with lime.

Para-isobutylorthohydroxybenzenecarboxylic acid, $(CH_3)_2C_2H_3.C_6H_3(OH)CO_2H$, is homologous with salicylic acid and is formed in a similar manner when the sodium compound of isobutylphenol is heated with carbon dioxide. It is scarcely soluble in cold, only slightly in hot water, from which it crystallizes in very fine, long, white lustrous needles, which are decomposed again into isobutylphenol and carbon dioxide by heating to 180°—190° with hydrochloric acid. Its aqueous solution is coloured deep violet by ferric chloride. The methyl ether crystallizes from wood-spirit in splendid, monosymmetric prisms, melts at 54° and boils at 266°.[4]

Parapropylphenylacetic acid or *Homocuminic acid*, $C_6H_4(C_3H_7)CH_2.CO_2H$, is a derivative of the still unknown propylethylbenzene. Its nitril is formed when cymyl chloride is heated with potassium cyanide and alcohol, and yields the acid on

[1] *Ber. Deutsch. Chem. Ges.* xvii. 1236.
[2] Gasiorowski and Merz, *ibid.* xviii. 1009.
[3] Kreysler, *ibid.* xviii. 1706.
[4] v. Dobrzycki, *Journ. Prakt. Chem.* [2] xxxvi. 389.

boiling with caustic potash. This crystallizes from hot water in small needles, melting at 52°.[1] On distillation with caustic lime, ordinary cymene is formed.[2]

THE PENTYLBENZENES.

2476 *Pentylbenzene*, $C_6H_5.C_5H_{11}$, has been obtained by Schramm by the action of sodium on a mixture of benzyl bromide and butyl bromide. It is a very pleasant smelling liquid, which boils at 200·5°—201·5° and has a sp. gr. of 0·8602 at 22°.[3]

Phenylpentoxylic acid, $C_6H_5.C_4H_8.CO_2H$, is formed when cinnamenylacrylic acid, $C_6H_5.CH{=}CH.CH{=}CH.CO_2H$, is heated to 160° with a saturated solution of hydriodic acid in glacial acetic acid. It is readily soluble in the usual solvents, with the exception of water, from which it crystallizes on cooling in plates, which melt at 58°—59°.[4]

Piperhydronic acid, $CH_2\begin{smallmatrix}O\\O\end{smallmatrix}C_6H_3.C_4H_8.CO_2H$, is obtained by the long-continued heating of β-hydropiperic acid with sodium amalgam and water, the liquid being kept neutral by the addition of hydrochloric acid. It may also be prepared, and apparently more readily, from β-bromohydropiperic acid. It crystallizes from dilute alcohol in small, thin tablets, which melt at 96°.[5]

Amylbenzene, $C_6H_5.C_2H_4.CH(CH_3)_2$, was prepared by Fittig and Tollens, who treated a solution of amyl bromide and bromobenzene in benzene with sodium.[6] A better yield is obtained when ether is used as a diluent instead of benzene (Schramm). It is also formed by the action of amyl chloride on a mixture of benzene and aluminium chloride[7] and is a pleasant smelling liquid, which boils at 193° and has a sp. gr. of 0·859 at 12°.

Tribromamylbenzene, $C_6H_2Br_3.C_5H_{11}$, crystallizes in needles, which melt at 140° and are readily soluble in hot alcohol (Bigot and Fittig).

[1] Rossi, *Ann. Chem. Pharm. Suppl.* i. 139.
[2] Paternò, *Ber. Deutsch. Chem. Ges.* xvii. Ref. 109.
[3] Schramm, *Ann. Chem. Pharm.* ccxviii. 383.
[4] Baeyer and Jackson, *Ber. Deutsch. Chem. Ges.* xiii. 122.
[5] Fittig and Buri, *Ann. Chem. Pharm.* ccxvi. 176.
[6] *Ann. Chem. Pharm.* cxxix. 369; cxxxi. 313; Bigot and Fittig, *ibid.* cxli. 160.
[7] Friedel and Crafts, *Ann. Chim. Phys.* [6] i. 454.

Amylphenol, $C_6H_4(OH)C_5H_{11}$, is formed when phenol, amyl alcohol and zinc chloride are heated together to 180°,[1] and crystallizes from hot water, in which it is only slightly soluble, in long needles, melting at 92°—93°. It boils at 255° and yields amylphenyl methyl ether, $C_6H_4(OCH_3)C_5H_{11}$, on heating with wood spirit, methyl iodide and caustic potash. This ether is a liquid, which boils at 216°—217° and is oxidized to anisic acid by chromic acid.[2]

Amylamidobenzene, $C_6H_4(NH_2)C_5H_{11}$, was obtained by Hofmann by heating amylaniline hydrochloride to 300°—340°.[3] It is also formed when amyl alcohol is heated to 270° with anilin and zinc chloride,[4] and is a liquid, which boils at 256°—258° and is converted by the diazo-reaction into amylphenol.

ω-Diethyltoluene or *Diethylphenylmethane*, $C_6H_5.CH(C_2H_5)_2$, is formed by the action of zinc ethyl on benzidene dichloride,[5] $C_6H_5.CHCl_2$, and benzenyl trichloride, $C_6H_5.CCl_3$, ethylene being simultaneously formed in each case.[6] It has also been prepared by heating diethylhomophthalic acid, $C_6H_4.C(C_2H_5)_2(CO_2H)_2$ with soda lime.[7] It is a liquid, which boils at 178°.

α-Ethyl-β-phenylpropionic acid or *Benzylbutyric acid*, $C_6H_5.CH_2.CH(C_2H_5)CO_2H$, is an oily liquid, which boils at 272° and is formed by the action of sodium amalgam and water on phenylangelic acid.[8]

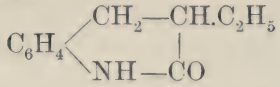
Benzyl benzylbutyrate, $C_6H_5.CH_2.CH(C_2H_5)CO_2.CH_2.C_6H_5$, is formed by the action of sodium on benzyl butyrate (Pt. IV. p. 98) and is a liquid, which boils at 330°—340°.[9]

Benzyl benzylisobutyrate, $C_6H_5.CH_2.C(CH_3)_2.CO_2.CH_2.C_6H_5$, has been prepared in a similar manner from benzyl isobutyrate; it boils at 285° and is resolved into toluene, isobutyric acid and benzoic acid on heating with soda lime to 200°.[10]

Ethylhydrocarbostyril, $C_{11}H_{13}NO$. Benzylbutyric acid yields an oily nitro-product, which is converted by reduction into ethylhydrocarbostyril (p. 169). This substance forms small

[1] Liebmann, *Ber. Deutsch. Chem. Ges.* xiv. 1842; xv. 150.
[2] Kreysler, *ibid.* xviii. 1706.
[3] *Ibid.* vii. 526.
[4] Merz and Weith, *ibid.* xiv. 2342; Calm, *ibid.* xv. 1462.
[5] Lippmann and Luginin, *Zeitschr. Chem.* 1867, 674.
[6] Dafert, *Monatsh. Chem.* iv. 153.
[7] Pulvermacher, *Ber. Deutsch. Chem. Ges.* xx. 2495.
[8] Baeyer and Jackson, *ibid.* xiii. 115.
[9] Conrad and Hodgkinson, *Ann. Chem. Pharm.* cxciii. 318.
[10] Hodgkinson, *Ann. Chem. Pharm.* cci. 166.

crystals, melting at 87°—88° and has the following constitution (Baeyer and Jackson):



Dimethylethylphenylmethane, $C_6H_5.C(C_2H_5)(CH_3)_2$, is formed by the action of aluminium chloride on a mixture of benzene and tertiary amylchloride or trimethylethylene, and is a liquid, which boils at 185°—190°.[1]

HYDROCARBONS, $C_{11}H_{14}$, AND THEIR DERIVATIVES.

2477 *Butenylmethylbenzene*, $CH_3.C_6H_4.CH_2.CH_2.CH=CH_2$, which is also called *tolylbutylene*, is obtained, together with diallyl and dixylyl, by the action of sodium on a mixture of allyl iodide and metaxylyl chloride. It is an aromatic smelling liquid, which boils at 195° and forms a liquid dibromide.[2]

Para-isopropylstyrolene, $(CH_3)_2CH.C_6H_4.CH=CH_2$, is formed when cumenylacrylic acid, $(CH_3)_2CH.C_6H_4.C_2H_2.CO_2H$, is heated, and by the action of sodium carbonate on bromohydrocumenylacrylic acid. It is an aromatic smelling liquid, which boils at 203°—204°, a considerable amount of para-isopropylmetastyrolene being thus formed and left behind.[3]

Para-isopropylstyrolene bromide, $(CH_3)_2CH.C_6H_4.CHBr.CH_2Br$, crystallizes from alcohol in lustrous needles melting at 71°.

Para-isopropylmetastyrolene, $(C_{11}H_{14})_n$, is formed, as stated above, by heating the hydrocarbon for some time to 150°, or when it is exposed to the light for one or two months. Like metastyrolene itself, it is a vitreous mass, which is reconverted into para-isopropylstyrolene by strongly heating.

Pentenylbenzene or *Phenylpentylene*, $C_6H_5.CH=CH.C_3H_7$. When bromine vapour is allowed to act upon pentylbenzene at 150°, the monobromide, $C_6H_5.C_5H_{10}Br$, is obtained and decomposes on distillation into hydrobromic acid and pentenylbenzene. It is a liquid, which boils at 210°—215.

[1] Essner, *Bull. Soc. Chim.* xxxvi. 212.
[2] Aronheim, *Ber. Deutsch. Chem. Ges.* ix. 1789.
[3] Perkin, *Journ. Chem. Soc.* 1877, i. 401; ii. 663.

Phenylpentenyl dibromide, $C_6H_5.C_5H_9Br_2$, forms needles or small plates, which melt at 53°—54°.[1]

Amenylbenzene or *Phenylamylene*, $C_6H_5.CH{=}CH.CH(CH_3)_2$, was obtained by Schramm in a similar manner from amylbenzene, as a liquid, boiling at 200·5°—201·5°.

Phenylamylene dibromide, $C_6H_5.C_5H_9Br_2$, is formed when the olefine is combined with bromine and also when amylbenzene is treated with bromine vapour at 150°. It crystallizes from hot alcohol in silky needles, which melt at 128°—129°.

Phenlyamylenglycol, $C_6H_5.CH(OH)CH(OH)CH(CH_3)_2$, is obtained by treating a mixture of benzaldehyde and isobutyraldehyde with alcoholic potash or sodium amalgam and separates from benzene in crystals, which have an aromatic odour and melt at 81°—82°.[2]

Phenylethylpropylene, $C_6H_5.CH(C_2H_5)CH{=}CH_2$. When diethylphenylmethane is treated at the boiling point with bromine, the compound $C_6H_5.CH(C_2H_5)CHBr.CH_3$, is formed as an oily liquid, the vapour of which attacks the eyes very violently, and which is converted into the olefine by boiling with water or alcoholic potash. The latter is a strongly refractive, pleasant smelling liquid and boils at 173°, being partially converted into *diphenylethylpropylene*, $C_{22}H_{28}$. This body boils at 208°—212° and does not combine with bromine, so that it probably has the following constitution:[3]

$$\begin{array}{l} C_6H_5.(C_2H_5)CH.CH.CH_2 \\ \qquad\qquad\qquad\quad | \quad\; | \\ C_6H_5.(C_2H_5)CH.CH.CH_2 \end{array}$$

HYDROXY-ACIDS, $C_{11}H_{14}O_3$.

2478 *Phenylpropylglycolic acid*, $C_6H_4(C_3H_7)CH(OH)CO_2H$, is formed by the action of hydrocyanic acid and hydrochloric acid on cuminaldehyde.[4] In order to prepare it, the aldehyde is diluted with ether, the necessary amount of powdered potassium cyanide added and the calculated quantity of fuming hydrochloric acid allowed to drop slowly into the well cooled mixture.

[1] Schramm, *Ann. Chem. Pharm.* ccxviii. 392.
[2] Fossek, *Monatsh. Chem.* v. 119.
[3] Dafert, *ibid.* iv. 616.
[4] Raab, *Ber. Deutsch. Chem. Ges.* viii. 1148.

The nitril is left after the evaporation of the ether as an oily liquid, which is converted into the acid by the action of cold, fuming hydrochloric acid.[1] The free acid crystallizes from water in small, white needles, melting at 158°.

Phenylhydroxylpivalic acid, $C_6H_5.CH(OH)C(CH_3)_2CO_2H$, is obtained by heating benzaldehyde with sodium isobutyrate and acetic anhydride or isobutyric anhydride and boiling the product, which consists of acetyl- or isobutyryl-phenylpivalic acid, with baryta water. It is only slightly soluble in cold, readily in hot water, from which it crystallizes in feathery groups of needles, which melt at 134° and decompose at 190° into carbon dioxide, water and butenylbenzene.[2]

It was stated in the discussion of the formation of cinnamic acid, that phenyl-lactic acid is probably formed as an intermediate product but immediately loses water. This view is confirmed by the formation of phenylhydroxypivalic acid, which cannot pass into a homologue of cinnamic acid by loss of water.

Benzylhydroxybutyric acid, $C_6H_5.CH_2.CH_2<\begin{matrix}CH(OH)CH_3\\CO_2H\end{matrix}$, is formed by the action of water and sodium amalgam on benzyl-acetoacetic ether (p. 358). It crystallizes on the evaporation of the alcoholic solution in thin prisms, whilst, when the hot aqueous solution is allowed to cool, the liquid becomes turbid and deposits a precipitate of hair like needles, melting at 152°—155°.[3]

Hydroxypiperhydronic acid, $C_{12}H_{14}O_5$, may be readily obtained by decomposing dibromopiperhydronic acid with alkalis:

$$CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_3.CH_2.CHBr.CHBr.CH_2.CO_2H + H_2O =$$

$$CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_3.CH_2.C(OH)=CH.CH_2.CO_2H + 2HBr.$$

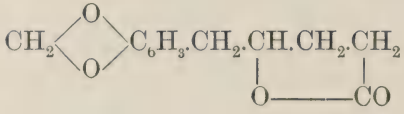
The hydroxy-acid thus formed passes immediately, as in analogous cases, into *piperoketonic acid*, $CH_2O_2.C_6H_3.CH_2.CO.CH_2.CH_2.CO_2H$, which crystallizes from hot water in long, thin needles, melting at 84°; the absence of an alcoholic hydroxyl is proved by the fact that the ethyl ether is not attacked by heating with acetic anhydride. On heating with sodium amalgam and

[1] Plöchl, *Ber. Deutsch. Chem. Ges.* xiv. 1316.

[2] Fittig and Jayne, *Ann. Chem. Pharm.* ccxvi. 115; Fittig and Ost, *ibid.* ccxxvii. 61.

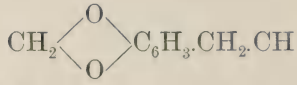
[3] Ehrlich, *ibid.* clxxxvii. 26.

water, it is converted into hydroxypiperhydronic acid, which separates from ether or hot water in lustrous crystals, melting at 95°. On further heating or on boiling with water, it is converted into *piperhydrolactone*, $C_{12}H_{12}O_4$, which is also formed when the acid is preserved in a desiccator. It is a clear, oily, tasteless and odourless liquid, which has the following constitution:[1]

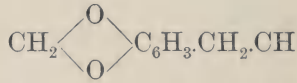


DIHYDROXY-ACIDS, $C_{11}H_{14}O$.

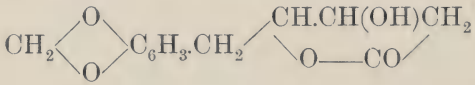
2479 Only the following derivatives of these bodies are known:

α-β-Dihydroxypiperhydronic acid, 

(OH)CH(OH).CO_2H, has been obtained by the action of potassium permanganate on *β*-hydropiperic acid. It is readily soluble in hot water and in alcohol, crystallizes in radiating groups of needles, melts at 165° and is converted by further oxidation into methylenehydrocaffeïc acid.

β-γ-Dihydroxypiperhydronic acid, 

(OH)CH(OH)CH_2.CO_2H, is formed by the oxidation of *α*-hydropiperic acid with potassium permanganate in alkaline solution and is precipitated by acids as *hydroxypiperhydrolactone*, which has the following constitution:



This substance is only slightly soluble in water, readily in alcohol and separates on the addition of petroleum spirit to its solution in chloroform in long, lustrous needles, which melt at 104·5°. If its solution in caustic potash be well cooled and acidified with dilute sulphuric acid, the dihydroxy-acid separates

[1] Fittig and Weinstein, *Ann. Chem. Pharm.* ccxxvii. 32.

out in fine, white crystals, which may be recrystallized from lukewarm water and melt at 123°, decomposing simultaneously into water and the lactone. It forms salts, which crystallize well and are very stable.[1]

KETONES, $C_{11}H_{14}O$.

2480 *Phenylbutylketone*, $C_6H_5.CO.C_4H_9$, is formed when propylbenzoylacetic ether, $C_6H_5.CO.CH(C_3H_7)CO_2.C_2H_5$, is boiled with alcoholic potash. It is an oily, aromatic smelling liquid, which boils at 236°—238°.[2]

Phenylisobutylketone, $C_6H_5.CO.C_2H_4(CH_3)_2$, was obtained by Popow by the distillation of a mixture of calcium benzoate and calcium valerate,[3] while Perkin and Calman prepared it from the ether of isopropylbenzoylacetic ether. It has also a pleasant aromatic odour, boils at 227°—228° and is oxidized by chromic acid to benzoic acid, isobutyric acid and acetic acid.

Xylylethylketone, $(CH_3)_2C_6H_3.CO.C_2H_5$, is formed by the action of aluminium chloride on a mixture of paraxylene and propionyl chloride. It is a strongly refractive, aromatic smelling liquid, which has a sharp, bitter taste and boils at 237°—238°.[4]

DIKETONES, $C_{11}H_{12}O_2$.

2481 *Phenylacetylacetone*, $C_6H_5.CH_2.CO.CH_2.CO.CH_3$, is obtained when phenylacetylaceto-acetic ether, $C_6H_5.CH_2.CO.CH(CO_2C_2H_5)CO.CH_3$, is boiled for some time with water. It is an oily liquid, which boils at 266°—269° and is tolerably soluble in hot water. If it be dissolved in dilute caustic soda and an excess of concentrated caustic soda solution added, the sodium salt separates out as a crystalline precipitate, while silver nitrate precipitates the compound $C_{11}H_{11}AgO_2$ from the ammoniacal solution in white flocks, which rapidly become violet coloured in the light.[5]

[1] Regel, *Ber. Deutsch. Chem. Ges.* xx. 414.
[2] Perkin and Calman, *Journ. Chem. Soc.* 1886, i. 161.
[3] *Ann. Chem. Pharm.* clxii. 153.
[4] Claus and Fickert, *Ber. Deutsch. Chem. Ges.* xix. 3182.
[5] Fischer and Bülow, *ibid.* xviii. 2136.

Acetophenone-acetone, $C_6H_5.CO.CH_2.CH_2.CO.CH_3$, is formed, when acetophenone-aceto-acetic ether, $C_6H_5.CO.CH_2.CH(CO_2C_2H_5)CO.CH_3$, is boiled with dilute alkalis. It is a yellowish oily liquid, which decomposes on heating and is only slightly soluble in cold, more readily in hot water.

Acetophenone-acetoxime, $C_{11}H_{12}O(NOH)$, is obtained by the action of hydroxylamine on the diketone and crystallizes from dilute alcohol in long, white, lustrous needles, which melt at 122°—123° and are soluble in both acids and alkalis.[1] If the ketone be heated with acetic anhydride or gently warmed with fuming hydrochloric acid, *phenylmethylfurfuran*, $C_{11}H_{10}O$, is formed, the ketone probably passing into the tautomeric alcohol, which then loses water:

$$\begin{array}{l} CH{=}C(OH).CH_3 \\ | \\ CH{=}C(OH).C_6H_5 \end{array} = \begin{array}{l} CH{=}C.CH_3 \\ |\quad >O \\ CH{=}C.C_6H_5 \end{array} + H_2O.$$

Phenylmethylfurfuran crystallizes from alcohol in long, lustrous needles, which have a faint odour of phenol and melt at 41°—42°. It boils at 235°—240° and is neither attacked by hydroxylamine nor acetyl chloride.[2] It is converted by the action of sodium upon its alcoholic solution into *phenylmethyltetramethylene oxide*, an oily, mobile liquid, which boils at about 230° and has the following constitution:

$$\begin{array}{l} CH_2.CH.CH_3 \\ |\quad >O \\ CH_2.CH.C_6H_5 \end{array}$$

KETONIC ACIDS.

2482 *Benzylaceto-acetic acid*, $CH_3.CO.CH(CH_2.C_6H_5)CO_2H$, is unknown in the free state. Its ethyl ether is formed by the action of benzyl chloride on sodium aceto-acetic ether and is a thick liquid, which has a faintly aromatic odour and boils at 276°.[3]

[1] Paal, *Ber. Deutsch. Chem. Ges.* xvi. 2865; xvii. 913.
[2] *Ibid.* xvii. 2756.
[3] Ehrlich, *Ann. Chem. Pharm.* clxxxvii. 12; Conrad and Bischoff, *ibid.* cciv. 180.

Dimethylbenzoylacetic acid, $(CH_3)_2C_6H_3.CO.CH_2.CO_2H$, has been prepared by the oxidation of paraxylylethylketone with potassium permanganate and is slightly soluble in water, readily in alcohol. It crystallizes from a mixture of petroleum ether and choloroform in fascicular groups of large needles, which melt at 132° (Claus and Fickert).

Ethylbenzoylacetic acid $C_6H_5.CO.CH(C_2H_5)CO_2H$, was obtained by Perkin, who dissolved 1·2 grams. of sodium in absolute alcohol, added 10 grams. of benzoylacetic ether to the cooled solution and boiled the mixture with 10 grams. of ethyl iodide. The ether thus obtained was saponified with cold alcoholic potash and the acid precipitated with dilute sulphuric acid. It forms crystals, which melt at 112°—115° with slight decomposition, and readily decomposes in an analogous manner to aceto-acetic ether (Pt. II. p. 175).[1]

The ethyl ether is a strongly refractive liquid, which has an aromatic odour and a burning taste, boils at 231°—232° at a pressure of 725 mm. and may be distilled at the ordinary pressure almost without decomposition when pure.[2]

Benzylacetone-orthocarboxylic acid, $CH_3.CO.C_2H_4.C_6H_4CO_2H$, is obtained by heating the carboxylic acid of benzylaceto-acetic ether, $CH_3.CO.CH(CO_2C_2H_5)CH_2.C_6H_4.CO_2H$, with baryta water, and crystallizes in fine needles, which are readily soluble in water and alcohol and melt at 114°.[3]

Phenyl-laevulinic acid, $C_6H_5.CH(CH_2.CO.CH_3)CO_2H$, is formed, when the ether of phenylacetosuccinic acid, $C_6H_5.CH(CH_3.COCH.CO_2H)CO_2H$, is boiled, and crystallizes from hot water in fascicular groups of pinnate plates, which melt at 126°.[4]

Benzoyltrimethylenecarboxylic acid, $C_6H_5.CO.C_3H_4.CO_2H$. The ethyl ether is obtained by adding ethyl benzoylacetate to a solution of sodium in absolute alcohol and then treating the cooled solution with ethylene bromide, the mixture being finally heated on the water bath:

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + 2CNaH\begin{matrix} CO.C_6H_5 \\ CO_2.C_2H_5 \end{matrix} =$$

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!C\begin{matrix} CO.C_6H_5 \\ CO_2.C_2H_5 \end{matrix} + CH_2\begin{matrix} CO.C_6H_5 \\ CO_2.C_2H_5 \end{matrix} + 2NaBr.$$

[1] Perkin, *Ber. Deutsch. Chem. Ges.* xvi. 2130.
[2] Perkin, *Journ. Chem. Soc.* 1885, i. 240.
[3] Bülow, *Ann. Chem. Pharm.* ccxxxvi. 192.
[4] Weltner, *Ber. Deutsch. Chem. Ges.* xvii. 72; xviii. 790.

The crude product is saponified with cold alcoholic potash and the acid separated by sulphuric acid and then purified by conversion into the sodium salt and reprecipitation.

Benzoyltrimethylenecarboxylic acid is only slightly soluble in water and crystallizes from ether in splendid, monoclinic prisms. It can be boiled with alcoholic potash without undergoing decomposition. The ethyl ether is a thick, oily liquid, which has a faint aromatic odour and a burning taste and boils without alteration at 280°—283°.

The acid melts with decomposition at 148°—149° and decomposes at a slightly higher temperature into carbon dioxide and *benzoyltrimethylene* $C_6H_5.CO.CH\begin{<}CH_2\\CH_2\end{>}$.

This is an oily, aromatic smelling liquid, which boils at 239°—239·5° and combines with hydroxylamine to form *benzoyltrimethylene-oxime*, $C_6H_5.C(NOH)C_3H_4$; this compound crystallizes from ether in well formed prisms, which melt at 86°—87° and decompose after standing for some time with formation of a brown oil.[1]

Benzoylaceto-acetic acid, $C_6H_5.CO.CH(CO_2H)CO.CH_3$. This diketonic acid is only known in the form of its ethyl ether, which is obtained by the action of benzoyl chloride on sodium aceto-acetic ether and is a thick liquid, which has a faint aromatic odour, decomposes on distillation[2] and is resolved into carbon dioxide, acetic acid, acetophenone and benzoylacetone by boiling with water or alcohol.[3]

Acetobenzalacetic acid or *a-Acetocinnamic acid* $C_6H_5.CH{=}C(CO.CH_3)CO_2H$. The ethyl ether is obtained by heating benzaldehyde with aceto-acetic ether and acetic anhydride. It distils as an odourless, strongly refractive, very thick liquid, solidifying after a short time to a macrocrystalline mass, which crystallizes from alcohol in very lustrous, transparent, four- or six-sided rhombic tablets. It melts at 59°—60° and boils at the ordinary pressure with slight decomposition at 295°—297°. A trace of this ether brought into sulphuric acid produces a light yellow solution, which becomes an opaque dark red on heating. If it be then poured into water, a yellow precipitate separates out, which forms a violet solution in caustic soda.

[1] Perkin, *Journ. Chem. Soc.* 1885, i. 836.
[2] Bonné, *Ann. Chem. Pharm.* clxxxvii. 1; James, *ibid.* ccxxvi. 220.
[3] E. Fischer and Bülow, *Ber. Deutsch. Chem. Ges.* xviii. 2131.

The ether is also formed when a mixture of benzaldehyde and aceto-acetic ether is saturated with hydrochloric acid at 0°. Two isomeric compounds, $C_{13}H_{15}ClO_3$, are the first products; these decompose on distillation with elimination of hydrochloric acid and may be separated by crystallization from boiling petroleum-spirit. The one crystallizes in prisms, which melt at 40°—41°, the other in small rhombohedra or tablets, melting at 71°—72°. Both decompose in moist air. Their formation admits of a simple explanation. Benzidene chlorhydrin is first formed and acts upon the ether:

$$C_6H_5.CH\begin{matrix}OH\\Cl\end{matrix} + CH_2\begin{matrix}CO.CH_3\\CO_2.C_2H_5\end{matrix} =$$

$$C_6H_5.CHCl.CH\begin{matrix}CO.CH_3\\CO_2.C_2H_5\end{matrix} + H_2O.$$

Hydrochloric acid is then eliminated and re-added, the isomeric compound being formed:[1]

$$C_6H_5.CH{=}C\begin{matrix}CO.CH_3\\CO_2.C_2H_5\end{matrix} + HCl = C_6H_5.CH_2.CCl\begin{matrix}CO.CH_3\\CO_2.C_2H_5\end{matrix}.$$

DIBASIC ACIDS.

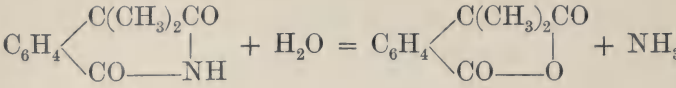
2483 *Dimethylhomophthalic acid*, $C_6H_4\begin{matrix}CO_2H\\C(CH_3)_2CO_2H\end{matrix}$. When a solution of homophthalimide, caustic potash and methyl iodide in wood spirit is heated to 100°, dimethyl homophthalimide is formed and has the following constitution:

$$C_6H_4\begin{matrix}C(CH_3)_2CO\\|\\CO\text{——}NH\end{matrix}$$

This substance crystallizes from hot water in flat, foliaceous needles, melting at 119°—120°. On heating with fuming

[1] Claisen and Matthews, *Ann. Chem. Pharm.* ccxviii. 176.

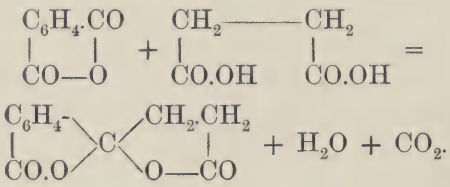
hydrochloric acid to 230°, the anhydride of dimethylhomophthalic acid is formed :



This body separates from alcohol in flat crystals, which melt at 82·5°—83° and dissolve slowly in ammonia. On addition of ammonia, *silver dimethylhomophthalate*, $C_{11}H_{10}Ag_2O_4$, is precipitated as a viscid mass, which becomes granular on boiling.[1]

Methylbenzylmalonic acid, $C_6H_5.CH_2.C(CH_3)(CO_2H)_2$, is formed by the action of methyl iodide on a solution of sodium and benzylmalonic ether in absolute alcohol. The ether thus obtained is a mobile liquid, which boils at 300° and is saponified by concentrated caustic potash solution. The free acid forms crystals, which melt at 135° and decompose at a higher temperature into methylbenzylacetic acid and carbon dioxide.

Benzoylpropionorthocarboxylic acid, $CO_2H.C_6H_4.CO.C_2H_4.CO_2H$. When phthalic anhydride is heated with succinic acid and sodium acetate, the double lactone of this acid is formed :



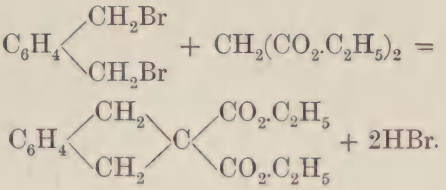
It crystallizes from alcohol in fine, lustrous needles, melting at 120°. On boiling with water, the acid is formed and remains on evaporation as a syrup, which has probably the composition $CO_2H.C_6H_4.C(OH)_2.C_2H_4.CO_2H$, and is re-converted into the lactone by heating on the water bath. If it be extracted with ether and the solution diluted with petroleum-ether, the benzoylpropionorthocarboxylic acid separates out in small, lustrous, six-sided prisms, which melt at 137°. Sodium amalgam converts it in alkaline solution into the acid, $CO_2H.C_6H_4.CH(OH)C_2H_4.CO_2H$ which, however, loses water and changes into *phthalidepropionic acid :*

[1] Gabriel, *Ber. Deutsch. Chem. Ges.* xix. 2363.

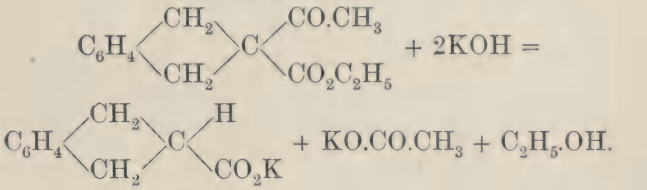
This substance crystallizes from hot water in nacreous plates, melting at 121°.[1]

On heating the lactone with hydriodic acid and phosphorus, *phenylbutyro-orthocarboxylic acid*, $CO_2H.C_6H_4.C_3H_6.CO_2H$, is formed and separates from the hot aqueous solution in small plates, melting at 138°—139°.[2]

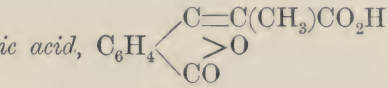
2484 *Hydrindonaphthenedicarboxylic acid*, $C_6H_4 : C_3H_4(CO_2H)_2$. The ethyl ether is formed by the action of orthoxylylene bromide on a solution of sodium and malonic ether in alcohol:



The free acid crystallizes from water in rhombic plates or tablets, which melt at 199° and decompose at a slightly higher temperature into carbon dioxide and *hydrindonaphthenemonocarboxylic acid*.[3] This is also formed when aceto-acetic ether is substituted for malonic ether in the above synthesis, and the acetyl derivative which is formed decomposed with caustic potash:



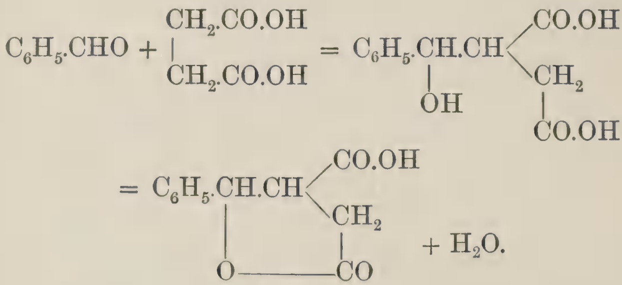
It crystallizes from boiling water in fascicular groups of needles, which melt at 130° and are volatile without decomposition. It is oxidized by potassium permanganate to the acid $C_6H_4(CO_2H)CO.CO_2H$, which yields phthalidecarboxylic acid on reduction.[4]

Phthalylpropionic acid,  , is obtained by boiling phthalic anhydride with sodium propionate and

[1] Roser, *Ber. Deutsch. Chem. Ges.* xvii. 2770.
[2] Roser, *ibid.* xviii. 3115.
[3] Baeyer and Perkin, *ibid.* xvii. 122.
[4] Scherks, *ibid.* xviii. 378; Perkin, *Journ. Chem. Soc.* 1888, i. 7.

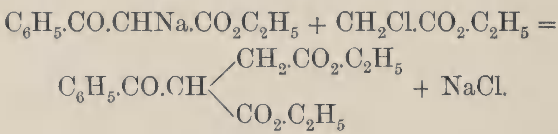
propionic anhydride, and crystallizes from alcohol in needles, melting at 245°—248°. It is converted into orthopropylbenzoic acid by heating with hydriodic acid, while boiling alkalis decompose it into carbon dioxide and propiophenonecarboxylic acid.[1]

Phenylparaconic acid, $C_{11}H_{10}O_4$, is formed, accompanied by a little isophenylcrotonic acid, when benzaldehyde is heated with sodium succinate and acetic anhydride :



The dibasic *phenylitamalic acid* is first formed, but decomposes immediately into water and its lactone, phenylparaconic acid. The latter crystallizes from hot water in long, lustrous needles of the formula, $4C_{11}H_{10}O_4 + H_2O$, which melt at 99°, lose their water and then melt at 109°. It combines in the cold with alkalis to form salts containing one equivalent of metal, while salts of phenylitamalic acid are obtained with hot solutions. These yield phenylparaconic acid on decomposition with acids. Phenylparaconic acid decomposes on dry distillation into carbon dioxide, phenylisocrotonic acid, phenylbutyrolactone and *a*-naphthol.[2]

Benzoylsuccinic acid, $C_6H_5.CO.CH(CO_2H)CH_2(CO_2H)$. The ethyl ether is readily formed by the action of ethyl monochloracetate on sodium benzoylacetic ether :



It is a thick, pleasant-smelling, aromatic liquid, which boils at 260°—265° at a pressure of 160 mm., and is coloured a fine

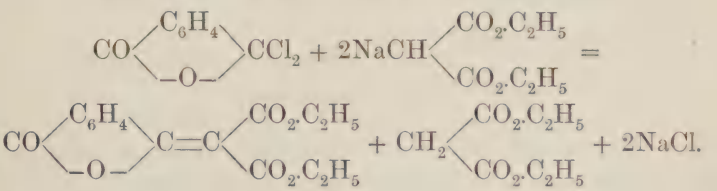
[1] Gabriel and Michael, *Ber. Deutsch. Chem. Ges.* xi. 1013.
[2] Fittig and Jayne, *Ann. Chem. Pharm.* ccxvi. 97.

claret-red in alcoholic solution by ferric chloride. When it is boiled with baryta water, benzoic and succinic acids are formed, while carbon dioxide and benzoylpropionic acid are obtained by boiling with sulphuric acid.[1]

Benzoylisosuccinic acid, $C_6H_5.CO.CH_2.CH(CO_2H)_2$. The ethyl ether is obtained by the action of benzoylmethyl bromide on sodmalonic ether, and is a heavy, yellow, oily liquid. The free acid crystallizes from water in spherical masses of small needles, melts and froths up at 178°—179°, and decomposes at a slightly higher temperature into carbon dioxide and benzoylpropionic acid.[2]

TRIBASIC ACIDS.

2485 *Benzylmalonorthocarboxylic acid*, $(CO_2H)_2CH.CH_2.C_6H_4.CO_2H$. The product of the action of phthalyl chloride on sodmalonic ether is *phthalylmalonic ether*:



It crystallizes from ether in large, asymmetric prisms, which show a large number of faces, have almost a diamond lustre and melt at 74·5°. It solidifies when pure in exceedingly characteristic forms; if a small quantity be fused on a watch glass and allowed to cool, the liquid commences to solidify at isolated spots and aggregates are formed, which absorb the residual liquid, so that finally a number of isolated masses, shaped like sea anemones, are formed.

The ether is decomposed by alkalis into malonic acid, phthalic acid and alcohol, while it yields diethyl benzylmalonorthocarboxylate on heating with zinc dust and acetic acid. This substance gives on saponification benzylmalonorthocarboxylic acid, which crystallizes from hot water in small, lustrous, very brittle prisms, which melt at 170° with evolution of carbon dioxide and decompose completely at 190° into this and hydrocinnamocarboxylic acid.

[1] Perkin, *Journ. Chem. Soc.* 1885, i. 272.
[2] Kues and Paal, *Ber. Deutsch. Chem. Ges.* xviii. 3323.

Diethyl benzylmalonorthocarboxylate, $(CO_2C_2H_5)_2CH.CH_2.C_6H_4.CO_2H$, which has been termed *benzylmalonic-ether-orthocarboxylic acid* by Wislicenus, is extremely soluble in ether, freely in alcohol and tolerably in hot water, from which it crystallizes in hair-like, pliable needles, melting at 86°.

It is a monobasic acid; its silver salt is energetically acted upon by ethyl iodide with formation of *triethyl benzylmalonorthocarboxylate*, $(C_2H_5.CO_2)_2CH.CH_2.C_6H_4.CO_2.C_2H_5$, which is a thick, colourless liquid, and boils at 250° at a pressure of 45 mm.[1]

Phenylcarboxysuccinic acid, $C_6H_5.CH(CO_2H)CH(CO_2H)_2$, is formed by the action of ethyl phenylchloracetate on sodium malonic ether and the saponification of the product. It forms readily soluble crystals and decomposes on heating into phenylsuccinic acid and carbon dioxide.[2]

ACIDS OF THE COMPOSITION, $C_6H_5.C_4H_6.CO_2H$.

2486 *Phenylangelic acid*, $C_6H_5.CH{=}C\begin{matrix}CH_2.CH_3\\ \\ CO.OH\end{matrix}$, was obtained by Perkin by heating benzaldehyde with butyric anhydride and sodium butyrate to 180°.[3] It is also formed when acetic anhydride is employed and the temperature not allowed to rise above 100°; at a higher temperature cinnamic acid is formed, the amount of this increasing with the temperature reached.[4]

Phenylangelic acid is only slightly soluble in water and separates from alcohol in compact, transparent crystals, which melt at 104°. Its chloride is a yellowish liquid, which is converted by ammonia into *phenylangelamide*, $C_6H_5.CH{=}C(C_2H_5)CO.NH_2$. This crystallizes from hot alcohol in prisms, melting at 128°.

Cinnamenylpropionic acid, $C_6H_5.CH{=}CH.CH_2.CH_2.CO_2H$, was prepared by Perkin,[5] who named it hydrocinnamenylacrylic acid, by the action of water and sodium amalgam on cinnamenylacrylic acid (p. 369). It is precipitated from solution in alkalis by hydrochloric acid as an oil, which solidifies in a freezing mixture, or at the ordinary temperature in contact with a portion of the

[1] Wislicenus, *Ann. Chem. Pharm.* ccxlii. 23.
[2] Spiegel, *ibid.* ccxix. 32.
[3] *Journ. Chem. Soc.* 1877, i. 393.
[4] Fittig and Slocum, *Ann. Chem. Pharm.* ccxxvii. 53.
[5] *Journ. Chem. Soc.* 1877, i. 405.

previously solidified acid, and crystallizes in large plates, which melt at 28°—29°.[1] It combines with bromine and hydrobromic acid, is not acted upon by sodium amalgam and is reduced to phenylpentylic acid by heating with hydriodic acid.

α-Hydropiperic acid, $CH_2\langle{}^{O}_{O}\rangle C_6H_3.CH_2.CH{=}CH.CH_2.CO_2H$,

was obtained by Foster, who dissolved piperic acid in caustic potash, heated the solution on the water bath with sodium amalgam and added hydrochloric acid from time to time.[2] It was then further investigated by Fittig in conjunction with Mielk,[3] Remsen,[4] and Buri.[5] The latter obtained an isomeric acid by this means which had not been previously observed, and which is only formed when the solution is kept strongly alkaline; sufficient hyrochloric acid must therefore be added in the preparation of the *α*-acid to keep the solution always faintly alkaline. The pure compound forms large, well developed crystals, which melt at 78°, and are slightly soluble in water, readily in alcohol. It is not further reduced by sodium amalgam and water, but combines with bromine to form *dibromopiperhydronic acid*, $CH_2{=}O_2.C_6H_3.CH_2.CHBr.CHBr.CH_2.CO_2H$, which separates from benzene in crystals, melting at 140°.[6] Potassium permanganate oxidizes *α*-hydropiperic acid to piperonal, piperonylic acid and hydroxypiperhydrolactone (p. 356).

β-Hydropiperic acid, $CH_2\langle{}^{O}_{O}\rangle C_6H_3.CH_2.CH_2.CH{=}CH.CO_2H$,

is not only formed as described above, but also when the *α*-acid is heated with caustic soda for some time. A hydroxypiperhydronic acid is probably first formed, in an analogous manner to the formation of hydracrylic acid from acrylic acid, but this loses water at the moment of liberation from its sodium salt and the position of the double linking is thus changed (Fittig and Weinstein):

$$CH_2\langle{}^{O}_{O}\rangle C_6H_3.CH_2.CH_2.CH(OH)CH_2.CO_2H =$$

$$CH_2\langle{}^{O}_{O}\rangle C_6H_3.CH_2.CH_2.CH{=}CH.CO_2H + H_2O.$$

[1] Baeyer and Jackson, *Ber. Deutsch. Chem. Ges.* xiii. 122.
[2] *Ann. Chem. Pharm.* cxxiv. 115.
[3] *Ibid.* clii. 56.
[4] *Ibid.* clix. 160.
[5] *Ibid.* ccxvi. 171.
[6] Fittig and Weinstein, *ibid.* ccxxvii. 33.

It crystallizes from alcohol in needles, melting at 131°, and combines with hydrogen to form piperhydronic acid (p. 351), but does not combine with bromine, which only yields substitution products. It is oxidized to dihydroxypiperhydronic acid by potassium permanganate (p. 356).

Bromo-β-hydropiperic acid, $CH_2O.C_6H_2Br.C_4H_6.CO_2H$, crystallizes from benzene in small, striated plates, melts at 170° —171° and is converted into bromomethylhydrocaffeïc acid by potassium permanganate.

Methylenedioxyphenylangelic acid, $CH_2\begin{<}O\\O\end{>}C_6H_3.CH{=}C(C_2H_5)CO_2H$, is formed when piperonal is boiled with butyric anhydride and sodium acetate. It crystallizes from alcohol in long, matted needles.[1]

COUMARINS, $C_{11}H_0O_2$.

2487 *Ethylcoumarin*, $C_6H_4\begin{<}CH{=}C(C_2H_5)\\O{-}CO\end{>}$, was obtained by Perkin, who named it *butyric-acid-coumarin* by heating sodium salicylaldehyde with butyric anhydride. It forms monosymmetric crystals, which smell like coumarin, melts at 70°—71°, boils at 299° with slight decomposition and is converted by boiling with caustic potash into *butyrocoumaric acid*, $C_6H_4(OH)CH{=}C(C_2H_5)CO_2H$, which crystallizes from dilute alcohol in flat prisms and melts at 174° with decomposition.[2]

Dimethylcoumarin, $CH_3.C_6H_3\begin{<}C(CH_3){=}CH\\O{-}CO\end{>}$, is formed by the action of sulphuric acid on a mixture of paracresol and acetoacetic ether and crystallizes from dilute alcohol in long, strongly refractive needles, melting at 148°.[3]

Dimethylcoumarilic acid, $CH_3.C_6H_3\begin{<}C{-}CH_3\\O\end{>}C.CO_2H$, is obtained by the action of hot, alcoholic potash on bromodimethylcoumarin (p. 246). It crystallizes from alcohol in short prisms or tablets

[1] Lorenz, *Ber. Deutsch. Chem. Ges.* xiv. 785.
[2] *Ann. Chem. Pharm.* cxlvii. 233; cl. 84; *Journ. Chem. Soc.* 1881, i. 439.
[3] von Pechmann and Duisberg, *Ber. Deutsch. Chem. Ges.* xvi. 2119; von Pechmann and Cohen, *ibid.* xvii. 2187.

which melt at 224°—225°. Its ethyl ether is analogous to that of the dimethylcoumarilic acid (p. 332), which has been prepared from paracresol and ethyl monochloraceto-acetate, melts at 55° and boils at 298°—300°.[1]

HYDROXYCOUMARINS, $C_{11}H_{10}O_3$.

2488 *Dimethylumbelliferon*, $C_6H_3(OH)\left\langle\begin{array}{l} C(CH_3)=C.CH_3 \\ \qquad\qquad\quad | \\ O\text{———}CO \end{array}\right.$, is formed by the action of sulphuric acid on a mixture of resorcinol and methylaceto-acetic ether. It crystallizes from wood-spirit in needles, which have a very high refractive index and melt at 256°. Its solutions in sulphuric acid and the alkalis are almost colourless, but show a distinct blue fluorescence.[2]

Homomethylumbelliferon, $CH_3.C_6H_2(OH)\left\langle\begin{array}{l} C(CH_3)=CH \\ \qquad\qquad\quad | \\ O\text{———}CO \end{array}\right.$, has been prepared from orcinol and aceto-acetic ether, and crystallizes from alcohol in needles, which melt and partially sublime at 248°—250°. It forms yellow, nonfluorescent solutions in sulphuric acid and the alkalis.[3]

ACIDS, $C_6H_5\,C_4H_4.CO_2H$.

2489 *Phenylbutinylcarboxylic acid*, $C_6H_5CH{=}CH.CH{=}CH.CO_2H$, was obtained by Perkin, who named it *cinnamenylacrylic acid*, by boiling cinnamaldehyde with sodium acetate and acetic anhydride.[4] When a mixture of cinnamaldehyde, malonic acid and glacial acetic acid is heated, *phenylbutinedicarboxylic acid*, $C_6H_5CH{=}CH.CH{=}C(CO_2H)_2$, is formed. This substance crystallizes in needles and decomposes on heating to 210° into carbon dioxide and phenylbutinylcarboxylic acid.[5] Acetone condenses with cinnamaldehyde in presence of dilute caustic soda solution to form *phenylbutinylmethylketone*, which crystallizes

[1] Hantzsch and Lang, *Ber. Deutsch. Chem. Ges.* xix. 1298.
[2] v. Pechmann and Duisberg, *ibid.* xvi. 2127.
[3] v. Pechmann and Cohen, *ibid.* xvii. 2189 ; Cohen, *Inaugur.-Dissert.*, Munich, 1884.
[4] *Journ. Chem. Soc.* 1877, i. 403.
[5] Stuart, *ibid.* 1886, i. 365.

in rhombic tablets, melting at 68°, and decomposes on heating with an alkaline solution of sodium hypochlorite into chloroform and the acid :[1]

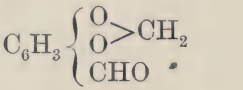
$$C_6H_5.CH{=}CH.CH{=}CH.CO.CH_3 + 3ClOH =$$
$$C_6H_5.CH{=}CH.CH{=}CH.CO_2H + CHCl_3 + 2H_2O.$$

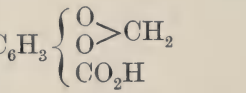
It crystallizes from alcohol, or better from petroleum ether, in thin tablets, melting at 166°.

Piperic acid, $C_{12}H_{10}O_4$, was discovered by v. Babo and Keller, who found that the piperine which is contained in pepper, decomposes on boiling with alcoholic potash into piperic acid and the volatile, strongly basic piperidine,[2] the reaction proceeding according to the following equation (Strecker) :[3]

$$C_{17}H_{19}NO_3 + H_2O = C_{12}H_{10}O_4 + C_5H_{11}N.$$

Piperic acid is almost insoluble in water and crystallizes from hot alcohol in long, yellowish, matted needles, which melt at 216°—217° and sublime with partial decomposition at a slightly higher temperature.[4] The constitution of this body has only been very gradually ascertained. Strecker found that the acid is monobasic and is decomposed by fusion with caustic potash into protocatechuic acid, oxalic acid and acetic acid,[5] while Foster showed that it combines with hydrogen to form hydropiperic acid, which is also monobasic (p. 367). Fittig and Mielck then proved that the two oxygen atoms, which are present in addition to those of the carboxyl group, are not contained in the form of hydroxyl, methoxyl or an homologous group. It is converted by oxidation with potassium permanganate into piperonal and piperonylic acid, the investigation of which led to the following formulæ, which were subsequently confirmed by the synthetical preparation of the substances in question :[6]

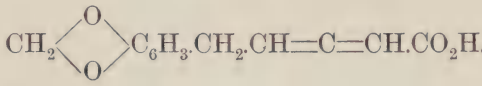




It was further observed that piperic acid combines with four atoms of bromine, and the following constitution was therefore ascribed to it :

[1] Diehl and Einhorn, *Ber. Deutsch. Chem. Ges.* xviii. 2324.
[2] *Jahresber. Chem.* 1857, 413.
[3] *Ann. Chem. Pharm.* cv. 217.
[4] Fittig and Mielck, *ibid.* clii. 25.
[5] *Ibid.* cxviii. 250.
[6] Fittig and Remsen, *ibid.* clix. 129 ; clxviii. 93.

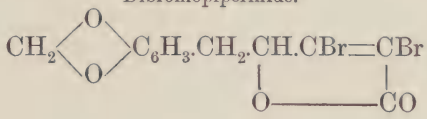
Since, however, the constitution of *a*-hydropiperic acid has now been ascertained with considerable accuracy, the formula given above must be rejected. It is known that acids of this class, such as *β*-hydropiperic acid for example, combine more readily with hydrogen the nearer the double linking is to the carboxyl group, and the constitution of piperic acid is therefore most probably represented by the formula:



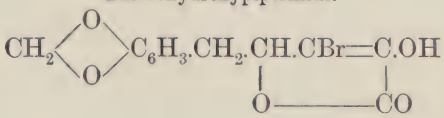
Ethyl piperate, $(CH_2O_2)C_6H_3.C_4H_4.CO_2.C_2H_5$, is formed when piperic acid is heated with ethyl iodide and caustic potash. It crystallizes from alcohol in large, yellowish, transparent, lustrous plates, melting at 77°—78°.

Tetrabromopiperhydronic acid, $(CH_2O_2)C_6H_3.C_4H_4Br_4.CO_2H$, is obtained by the action of bromine on piperic acid in presence of carbon disulphide, and is a crystalline powder, which melts at 160°—165° and decomposes energetically at the same time. On boiling with water or on dissolving in cold sodium carbonate solution, *dibromopiperinide*, $C_{12}H_8Br_2O_4$, is formed, which crystallizes from dilute alcohol in lustrous prisms, melting at 136°, and is converted by boiling with sodium carbonate solution into *bromohydroxypiperinide*, $C_{12}H_9BrO_5$. This substance separates from alcohol in monosymmetric crystals and decomposes on further boiling with alkalis with formation of piperonal.[1] The constitution of these compounds is probably expressed by the following formulæ:

Dibromopiperinide.



Bromohydroxypiperinide.



[1] Fittig and Mielck, *Ann. Chem. Pharm.* clxxii. 134.

INDOL DERIVATIVES CONTAINING ELEVEN ATOMS OF CARBON.

2490 *Pr*2-3-*Methylethylindol*, $C_6H_4\langle^{C—C_2H_5}_{NH}\rangle C.CH_3$, is formed when methylpropylketone hydrazone is heated with zinc chloride, and is an oily liquid, which boils at 291°—293°. Its picrate crystallizes from benzene in fine, dark red needles.

Acetylmethylketol is obtained when methylketol is heated with sodium acetate and acetic anhydride, in a similar manner to pseudo-acetylpyrrol (Pt. II. p. 611).

$$C_6H_4\langle^{CH}_{NH}\rangle C.CH_3 + O\langle^{CO.CH_3}_{CO.CH_3} = C_6H_4\langle^{C.CO.CH_3}_{NH}\rangle C.CH_3 + HO.CO.CH_3.$$

It crystallizes from benzene in colourless needles, melting at 195°—196°, and forms a hydrazone.[1]

*Pr*2-3-*Methylindolacetic acid*, $C_6H_4\langle^{C—CH_2.CO_2H}_{NH}\rangle C.CH_3$, has been obtained from lævulinic acid hydrazone and is slightly soluble in hot water, readily in alcohol. It separates from acetone in crystals, which show a large number of faces, melt at 195°—200° with energetic evolution of carbon dioxide and decompose completely on heating into this and Pr2-3-dimethylindol (p. 340). It does not give the pine-wood reaction, but forms a picrate, which crystallizes in dark red needles.

*Pr*1^n-2-3-*Dimethylindolacetic acid*, $C_6H_4\langle^{C—CH_2.CO_2H}_{N.CH_3}\rangle C.CH_3$, has been prepared from methylphenylhydrazine and lævulinic acid, and crystallizes in fine, colourless plates, which melt at about 180° and decompose when more strongly heated into carbon dioxide and Pr1^n-2-3-trimethylindol. The picrate forms red, feathery aggregates.[2]

[1] Jackson, *Ber. Deutsch. Chem. Ges.* xiv. 879 ; E. Fischer, *Ann. Chem. Pharm.* cxlii. 378.

[2] Degen, *ibid.* ccxxxvi. 151.

MELLITENE GROUP.

2491 The first compound of this group which was known to chemists was mellitic acid, and the corresponding hydrocarbon was, therefore, named mellitene.

HYDROCARBONS, $C_{12}H_{18}$, AND THEIR DERIVATIVES.

Hexmethylbenzene or Mellitene, $C_6(CH_3)_6$.

This substance was first obtained by Hofmann, together with other products, by heating trimethylphenylammonium iodide to 330°.[1] He also found that it is formed when xylidine hydrochloride is heated to 250°—300° with wood-spirit.[2] Lebel and Greene obtained it in small quantity, accompanied by other products, by heating wood-spirit strongly with zinc chloride, and the latter chemist prepared it in the same way from acetone.[3] It was prepared in larger quantity by Crafts and Friedel by the action of methyl chloride on a mixture of aluminium chloride and benzene or toluene.[4] The polymerization of crotonylene, $CH_3.C{\equiv}C.CH_3$, to hexmethylbenzene, which is brought about by agitation with sulphuric acid, is especially interesting.[5] Its formation from durene has already been mentioned (p. 343). It is remarkable that both mellitene and trichloromesitylene are formed when methyl chloride is passed into a heated mixture of orthodichlorobenzene and aluminium chloride. The chlorine is probably replaced by the aluminium chloride residue and then

[1] *Ber. Deutsch. Chem. Ges.* v. 720.
[2] *Ibid.* xiii. 1729.
[3] *Compt. Rend.* lxxxvi. 260 and 930.
[4] *Ann. Chim. Phys.* [6] i. 459.
[5] *Ber. Deutsch. Chem. Ges.* xiv. 2073.

forms substitution products with the mesitylene which is also formed in the reaction.[1]

Mellitene is readily soluble in hot alcohol and crystallizes in flat prisms or rhombic tablets, melts at 164°, boils at 264°, and, since it does not form a sulphonic acid, is insoluble in sulphuric acid. It can therefore be readily separated from pentamethylbenzene. On heating to 200° with aluminium chloride, pentamethylbenzene, durene, isodurene, mesitylene, pseudocumene, metaxylene and very small quantities of toluene and benzene are formed, these being obtained in larger amount when hexmethylbenzene is heated with aluminium chloride in a current of hydrochloric acid.[2]

It combines with picric acid to form the compound $C_6(CH_3)_6 + C_6H_3(NO_2)_3O$, which crystallizes in golden yellow flakes, melting at 168°—169°.

Mellitone hexchloride or hexchloromellitene, $C_6(CH_2Cl)_6$, is formed when the hydrocarbon is heated with phosphorus pentachloride. It crystallizes in flat, hexagonal tablets and melts and partially sublimes at 269°. When it is boiled with very dilute caustic soda solution, the chlorine is gradually removed and a substance is formed which melts at 180° and yields an aqueous solution, which has a very bitter taste. An isomeric compound is also formed in the preparation of hexchloromellitene; it melts at 147° and probably has the formula $C_6(CH_3)_2(CH_2Cl)_3CCl_3$.[3]

Mellitone hexbromide or *hexbromomellitene*, $C_6(CH_2Br)_6$, is formed when mellitene is heated to 115°—120° with bromine and a little water, and is insoluble or only slightly soluble in most solvents. It crystallizes from ethylene bromide in rhombic tablets, which melt at 255°.[4]

MELLITIC ACID, $C_6(CO_2H)_6$.

2492 This acid was discovered in the year 1799 by Klaproth, who obtained it by boiling honeystone with water for a considerable length of time, and named it *honeystone acid*. He compared it with the vegetable acids, but was naturally unable

[1] Friedel and Crafts, *Ann. Chim. Phys.* [6] x. 411.
[2] Jacobsen, *Ber. Deutsch. Chem. Ges.* xviii. 338.
[3] Colson, *Bull. Soc. Chim.* xlvi. 197.
[4] Hofmann, *Ber. Deutsch. Chem. Ges.* xiii. 1729; Friedel and Crafts, *Ann. Chim. Phys.* [6] i. 468.

at that early date to determine its nature. We owe to him, however, an experiment, which guided a later investigator to this end. He submitted honeystone, which is the aluminium salt of mellitic acid and occurs in seams of brown-coal, to dry distillation and obtained, together with carbon dioxide and a gas, which must have been carbon monoxide, a large quantity of water, which had simultaneously a pleasant, flowery odour and one of bitter almonds, and a drop of oil, which had a similar but fainter odour.

The honeystone acid (*acide mellitique*) was then investigated by Vauquelin, but Wöhler observed that this chemist had mistaken the acid potassium salt for the acid, and that Klaproth's acid had been rendered impure by the presence of alumina. He prepared the pure compound and found that it decomposes on heating and yields a crystalline sublimate, without producing an empyreumatic odour like other organic acids, but resembles oxalic acid in its other properties. According to him, honeystone contains a trace of a characteristic, apparently resinous substance, which was also noticed by Klaproth; this is the cause of the aromatic smell produced when honeystone is burnt and is contained in all the salts prepared from it.[1] Liebig and Wöhler determined the formula for honeystone as $C_4H_2O_4$ and believed that it might possibly be formed from succinic acid, which also occurs in brown-coal. They even attempted to convert succinic into mellitic acid by the action of chlorine, an experiment which, occurring at that early period, is of special interest:[2]

$$C_4H_6O_4 + 4Cl = C_4H_2O_4 + 4HCl.$$

Erdmann, who found that mellitic acid is converted into pyromellitic acid by heating, observed that a characteristic spicy odour, resembling that of coumarin and oil of Spiræa, is produced when the salts of mellitic acid are heated. He therefore heated a considerable quantity of the copper salt and obtained a solid substance and a liquid, which smelt like oil of bitter almonds or oil of cinnamon, and which he compared with the products obtained by the distillation of copper benzoate and copper salicylate by Ettling and Stenhouse. By the distillation of calcium mellitate, he only obtained a small quantity of an aromatic vapour.

[1] *Pogg. Ann.* vii. 325.

[2] *Ibid.* xviii. 161.

The analysis of the substances mentioned above proved that they contained hydrogen; since however this element is not present in the dried, anhydrous mellitates, the decomposition, which occurs when these salts, which are difficult to prepare in the anhydrous state, are heated, is "one in which both the elements of mellitic acid and of water take part."[1] These results obviously show that aromatic substances are formed when mellitic acid is decomposed by heat, but these were only obtained in small quantity by Erdmann because sufficient hydrogen was not present. Baeyer therefore heated the acid with soda-lime and obtained a considerable quantity of benzene. He says on this point: "According to the formula $C_4H_2O_4$, which was then universally accepted, I had to await the evolution of acetylene, just as ethyl hydride is obtained by igniting succinic acid with lime:

$$C_4H_6O_4 = C_2H_6 + 2CO_2$$
$$C_4H_2O_4 = C_2H_2 + 2CO_2.$$

"When I obtained benzene, I at first thought that a condensation of the acetylene had taken place at the high temperature employed, this having been recently observed by Berthelot, when this gas is kept at a red-heat for some time. If this had been the case, mellitic acid ought to have yielded an isomeride of fumaric or succinic acid on reduction:

$$C_4H_2O_4 + H_2 = C_4H_4O_4$$
$$C_4H_2O_4 + H_4 = C_4H_6O_4.$$

"On treatment with sodium amalgam, however, mellitic acid was converted into an acid, which did not volatilize on heating, but carbonized like sugar and at the same time produced a smell of burnt sugar. Mellitic acid must, therefore, have a much more complicated composition than had hitherto been believed, and it appeared probable that the products of its decomposition with soda-lime are not formed by condensation but are rather portions of a single molecule. According to this view, the simplest formula for mellitic acid is $C_{12}O_{12}H_6$ and it is a benzene in which all the hydrogen atoms have been replaced by carboxyl groups, CO.OH. The formula $C_6(CO_2H)_6$ shows its analogy to benzoic acid, and its decomposition on heating with

[1] *Journ. Prakt. Chem.* lii. 432.

lime corresponds exactly to the decomposition of benzoic acid into carbon dioxide and benzene:

$$C_6H_5(CO_2H) = C_6H_6 + CO_2$$
$$C_6(CO_2H)_6 = C_6H_6 + 6CO_2.$$

"It is, further, the final member of a series of acids, several of which are already known, the so-called aromatic acids, which arise through the displacement of one or more hydrogen atoms in benzene by carboxyl." [1]

The line of investigation to pursue with respect to mellitic acid was thus indicated. All these acids, which have already been described, should be obtained in succession by the gradual elimination of carbon dioxide, and, with the exception of benzenepentacarboxylic acid, this proved to be the case. The observations of the earlier investigators were now fully explained. Baeyer repeated Klaproth's experiment and states that the smell produced can easily be identified with that of the benzene obtained by distilling benzoic acid with lime, which is always mixed with oil of bitter almonds, diphenyl and probably other bodies. The products which Erdmann obtained also consisted of a mixture of benzene with aldehydes or ketones, which could not be formed if absolutely anhydrous salts of mellitic acid were employed, since these undergo the following decompositions:

$$C_{12}O_{12}Cu_3 = 3Cu + 12CO$$
$$C_{12}O_{12}Ca_3 = 3CaCO_3 + 3CO + 6C$$
$$C_{12}O_{12}Al_2 = Al_2O_3 + 9CO + 3C.$$

The formation of mellitic acid from wood charcoal and other kinds of amorphous carbon, which was discovered by Schulze, is especially remarkable. If these be oxidized with an alkaline solution of potassium permanganate, oxalic and mellitic acids [2] are obtained in considerable quantity, together with other products. They are also formed in small quantity, accompanied by hydromellitic acid and pyromellitic acid, when a current of electricity is passed through a solution of caustic potash between carbon poles,[3] a fact which renders it possible that the benzene ring is contained in amorphous carbon. Mellitic acid is perhaps formed in nature by the oxidation of brown-coal. Friedel and

[1] *Ann. Chem. Pharm. Suppl.* vii. 1.
[2] *Ber. Deutsch. Chem. Ges.* iv. 802 and 806.
[3] Bartoli and Papasogli, *Gaz. Chim. Ital.* xiii. 37.

Crafts obtained it by oxidizing hexmethylbenzene with alkaline potassium permanganate. In order to prepare mellitic acid, Wöhler brought the finely powdered honeystone into a solution of ammonium carbonate, which was thus decomposed with evolution of carbon dioxide, boiled the solution until the excess of ammonia was removed, filtered off the hydrated alumina and allowed the ammonium mellitate to crystallize out. The pure salt was then dissolved in water and precipitated with lead acetate, the precipitate being well washed, suspended in water and decomposed by sulphuretted hydrogen. According to Erdmann and Marchand, the lead precipitate always contains ammonia, and in order to obtain an acid quite free from ammonia it is necessary to boil the ammonium salt with baryta and decompose the barium salt with sulphuric acid.[1] If the original honeystone be black and earthy, it must be digested for a considerable time with concentrated ammonia at a gentle heat, and the liquid finally heated to boiling and filtered off. The dark coloured filtrate is then evaporated to dryness and the residue heated for several hours to 120°—130°. Boiling water then extracts pure acid ammonium mellitate, to which Wöhler's method can subsequently be applied.[2]

Mellitic acid has a strongly acid taste, is extremely soluble in water and remains on evaporation as an indistinct crystalline powder. It is also readily soluble in alcohol and crystallizes on evaporation in stellate groups of fine needles. It is not attacked by boiling sulphuric acid, concentrated nitric acid, chlorine, bromine or hydriodic acid. On dry distillation it decomposes into carbon dioxide and pyromellitic acid, $C_6H_2(CO_2H)_4$, while on heating with glycerol, it yields trimesic acid, $C_6H_3(CO_2H)_3$.

2493 Its salts have been chiefly investigated by Erdmann and Marchand, as well as by Kamrodt.[3] They are very numerous, since mellitic acid is hexbasic, and their constitution was first explained by Baeyer.

Normal potassium mellitate, $C_{12}O_{12}K_6 + 9H_2O$, forms large, rhombic crystals, which readily effloresce. The acid salt, $C_{12}O_{12}H_3K_3 + 6H_2O$, crystallizes in large, rhombic prisms, which lose their water and become milk-white at a gentle heat. Wöhler, by the addition of nitric acid to a solution of the

[1] *Journ. Prakt. Chem.* xliii. 129.
[2] Claus, *Ber. Deutsch. Chem. Ges.* x. 560.
[3] *Ann. Chem. Pharm.* lxxxi. 164.

normal salt, obtained a precipitate resembling cream of tartar, which he considered to be the acid salt. It is however a double salt, $C_{12}O_{12}H_3K_3 + NO_3K$, and crystallizes from hot water in irregular six-sided prisms.

Normal ammonium mellitate, $C_{12}O_{12}(NH_4)_6 + 9H_2O$, is isomorphous with the potassium salt; the acid salt, $C_{12}O_{12}H_4(NH_4)_2 + 4H_2O$, crystallizes in rhombic prisms.

Barium mellitate, $C_{12}O_{12}Ba_3 + 3H_2O$, is precipitated in fine needles, when dilute solutions of ammonium mellitate and a barium salt are mixed. After drying it forms a silvery, foliaceous mass, which is only very slightly soluble in water.

Silver mellitate, $C_{12}O_{12}Ag_6$, is a crystalline precipitate, which only decomposes at above 130°.

The mellitates of most of the metals are obtained as slightly soluble or insoluble precipitates. If the ammonium salt be precipitated with copper sulphate, the salt, $C_{12}O_{12}Cu_2(NH_4)_2$, separates out in sky-blue, microscropic crystals.

Aluminium mellitate, $C_{12}O_{12}Al_2 + 18H_2O$, occurs as *honeystone* or *mellite* in brown coal seams and forms in the pure state honey-yellow, transparent quadratic pyramids, which have a fatty lustre. It generally contains a small percentage of iron and is also found more or less darkly-coloured and as a black, earthy mass.

Methyl mellitate, $C_{12}O_{12}(CH_3)_6$, has been obtained by Kraut by the action of methyl iodide on silver mellitate,[1] while H. Müller prepared it by heating wood-spirit with mellityl chloride.[2] It separates on the addition of water to its alcoholic solution in small lustrous plates, melting at 187°.[3]

Ethyl mellitate, $C_{12}O_{12}(C_2H_5)_6$, forms rhomboidal crystals, which melt at 73° (Kraut and Busse).

Mellityl chloride, $C_6(COCl)_6$, is formed when the acid is heated with phosphorus pentachloride and crystallizes from ether or benzene in hard, vitreous prisms, which melt at 190° and sublime in small plates at about 240°. It is only slowly decomposed by boiling water (Baeyer; Claus).

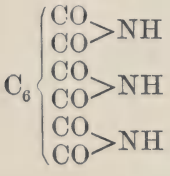
Imido-compounds of mellityl. By heating ammonium mellitate, Wöhler obtained *paramide*, C_4HNO_2, together with the ammonium salt of *euchronic acid*, $C_{12}H_4N_2O_8$, to which he gave this name because it is converted by reduction into a deep blue

[1] *Jahresber. Chem.* 1862, 281.
[2] H. Müller, *Kekulé's Lehrb.* ii. 405.
[3] Kraut and Busse, *Ann. Chem. Pharm.* clxxvii. 273.

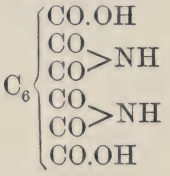
substance, *euchron*.[1] Schwarz then found that, when the freshly prepared solution of paramide in ammonia is decomposed with hydrochloric acid, *paramidic acid*, $C_{12}H_5N_3O_7$, is precipitated.[2]

The constitution of these compounds was quite unknown until Baeyer had explained that of mellitic acid :

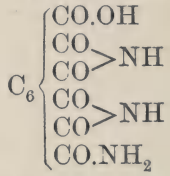
Paramide.



Euchronic acid.



Paramidic acid.



Paramide or *Mellitimide* forms a white, tasteless and odourless mass, which on trituration with water takes the smell and consistency of moist clay (Wöhler). It is insoluble in water, alcohol and aqua regia, and dissolves without decomposition in sulphuric acid. It is converted by alkalis into euchronic acid and mellitic acid, the latter of which is also formed when it is heated to 200° with water.

Argentammonium mellitimide, $C_6(CO)_6(NAgNH_3)_3$, is obtained as a precipitate when silver nitrate is added to a freshly prepared solution of paramide in ammonia. It dries to a yellow mass.

Euchronic acid or *Mellitiminic acid* is very difficultly soluble in water and crystallizes from hot, dilute hydrochloric acid in small, four-sided prisms, which taste like cream of tartar. When its solution is treated with zinc, the deep-blue coloured euchrone separates out. It forms a splendid purple-coloured solution in alkalis and rapidly reoxidizes to euchronic acid in the air. Its composition is unknown, but, owing to the ease with which it is formed, it serves as a delicate test for the presence of mellitic acid. When euchronic acid is heated with water to 200°, it is converted into acid ammonium mellitate.

Paramidic acid or *Amidomellitiminic acid* is a snow-white, crystalline powder, which is only slightly soluble in hot water, gives the euchrone reaction with zinc and is gradually converted into mellitic acid in ammoniacal solution.

Hydromellitic acid, $C_6H_6(CO_2H)_6$, is readily formed by the action of sodium amalgam and water on ammonium mellitate.

[1] *Ann. Chem. Pharm.* xxxvii. 268. [2] *Ibid.* lxvi. 46.

In order to prepare the acid from the product thus obtained, acetic acid is added, the solution precipitated with lead acetate and the precipitate decomposed by sulphuretted hydrogen. The hydromellitic acid remains on evaporation as a syrup, which gradually solidifies to indistinct crystals. It is strongly acid, melts on heating, then becomes brown and evolves carbon dioxide and finally decomposes with carbonization and evolution of fumes, which smell like the products which pass over last in the dry distillation of citric acid. It is scarcely attacked by oxidizing agents or a mixture of nitric and sulphuric acids. On heating with sulphuric acid, trimesic acid, prehnitic acid, mellophanic acid and prehnomalic acid are formed (p. 282).

Isohydromellitic acid, $C_6H_6(CO_2H)_6$, is gradually formed when hydromellitic acid is preserved, and more rapidly when it is heated to 180° for several hours with strong hydrochloric acid. It is tolerably soluble in water and crystallizes in hard, fairly large, thick, four-sided prisms, which melt and carbonize on heating. It is not attacked by hydrochloric acid even at 300° or by boiling with a mixture of sulphuric and nitric acids. Potassium permanganate only attacks it very slowly, while it is oxidized to carbon dioxide and acetic acid by heating with chromic acid solution. On heating with sulphuric acid, it yields the same products as hydromellitic acid.

Methyl isohydromellitate, $C_6H_6(CO_2.CH_3)_6$, is formed by the action of methyl iodide on the silver salt, which is a fine granular precipitate. It crystallizes in needles, which melt at 125° and are insoluble in water, but dissolve readily in alcohol (Baeyer).

The cause of the isomerism of these two acids is unknown.

s-TRIETHYLBENZENE, $C_6H_3(C_2H_5)_3$.

2494 Jacobsen prepared this hydrocarbon by the distillation of a mixture of acetone and methylethylketone with sulphuric acid,[1] while Friedel and Balsohn obtained it by the action of ethylene on a mixture of aluminium chloride and benzene.[2] It is a liquid, which boils at 214°—218°, and is converted by oxidation into trimesic acid.

[1] *Ber. Deutsch. Chem. Ges.* vii. 1430.
[2] *Bull. Soc. Chim.* xxxi. 540 ; xxxiv. 635.

DIPROPYLBENZENES.

Paradipropylbenzene, $C_6H_4(C_3H_7)_2$, has been obtained by the action of sodium on a mixture of paradibromobenzene and propyl bromide. It is a strongly refractive liquid, which smells like sassafras oil and boils at 218°—220°. It is oxidized by dilute nitric acid to parapropylbenzoic acid.

Dibromoparadipropylbenzene, $C_6H_2Br_2(C_3H_7)_2$, is formed by the action of bromine on the hydrocarbon in the cold and crystallizes from alcohol in lustrous needles or rectangular prisms, melting at 48°.

Dinitroparadipropylbenzene, $C_6H_2(NO_2)_2(C_3H_7)_2$, separates from alcohol in large, colourless, rectangular tablets, which become yellow in the air, and melt at 65°.[1]

Propylisopropylbenzene, $C_3H_7.C_6H_4.CH(CH_3)_2$, has been obtained by the action of zinc ethyl on cymyl chloride and is a liquid, which boils at 211°—213° and is oxidized by dilute nitric acid to propylbenzoic acid and bromoterephthalic acid.[2]

Di-isopropylbenzene, $C_6H_4[CH(CH_3)_2]_2$, was prepared by Silva by the action of aluminium chloride on a mixture of benzene and propyl chloride or isopropyl chloride (p. 153), as a pleasant smelling liquid, which boils at 202°—206°.[3]

AMYLTOLUENES, $CH_3.C_6H_4.C_3H_5(CH_3)_2$.

Para-amyltoluene is formed by the action of sodium on a mixture of parabromotoluene and amyl bromide, and is a pleasant smelling liquid, which boils at 213°. It is converted into terephthalic acid by chromic acid solution, while nitric acid yields liquid substitution products.[4]

Meta-amyltoluene is the product of the action of aluminium chloride on a mixture of toluene and amyl chloride or amylene. It is a liquid, which has an aromatic odour, somewhat resembling that of camphor, boils at 207°—209° and yields isophthalic acid on oxidation.[5]

[1] Körner, *Ann. Chem. Pharm.* ccxvi 223.
[2] Paternò and Spica, *Ber. Deutsch. Chem. Ges.* x. 1746.
[3] *Bull. Soc. Chim.* xliii. 320.
[4] Fittig and Bigot, *Ann. Chem. Pharm.* cxli. 162.
[5] Essner and Gossin, *Bull. Soc. Chim.* xlii. 213.

ISOHEXYLBENZENE, $C_6H_5.C_4H_7(CH_3)_2$.

This substance has been obtained by acting upon a mixture of amyl bromide and benzyl chloride with sodium. It is a pleasant smelling liquid, which boils at 212°—213°, and behaves in a similar manner to pentylbenzene (p. 351) when heated with bromine.[1]

ACIDS OF THE FORMULA $C_{12}H_{16}O_2$.

2495 *Cumenylpropionic acid*, $C_3H_7.C_6H_4.C_2H_4.CO_2H$, is formed when cumenylacrylic acid is heated with hydriodic acid and phosphorus. It crystallizes in plates, melting at 75·5°, and is converted by concentrated nitric acid into two orthonitro-acids, one of which probably contains the propyl, the other the isopropyl-group.

Cumenylbromopropionic acid, $C_3H_7.C_6H_4\,C_2H_3Br.CO_2H$, is obtained by the combination of hydrobromic acid with cumenylacrylic acid, and crystallizes from ether in lustrous prisms, melting at 85°—87°.[2]

Metamidocumenylpropionic acid, $C_3H_7.C_6H_3(NH_2)C_3H_5O_2$, is formed by the action of sodium amalgam on an alkaline solution of metamidocumenylacrylic acid and crystallizes from ether in long, pointed tablets, which melt at 102°—103°.[3]

Propylhydrocarbostyril, $C_3H_7.C_6H_3\left\langle\begin{array}{l}CH_2.CH_2\\ \quad\;\;|\\ NH.CO\end{array}\right.$, is obtained by heating the mixture of orthonitro-acids with zinc and hydrochloric acid, but may be more easily prepared from cumenylacrylic acid (p. 389). It is readily soluble in alcohol and separates from benzene on the addition of ligroïn in rhombic tablets or prisms, which melt at 134°.[4]

Amylbenzoic acid, $(CH_3)_2C_3H_5.C_6H_4.CO_2H$. The nitril of this acid is formed when amylphenyl phosphate, $(C_5H_{11}.C_6H_4)_3PO_4$, is

[1] Aronheim, *Ann. Chem. Pharm* clxxi. 223 ; Schramm, *ibid.* ccxviii. 391.
[2] Perkin, *Journ. Chem. Soc.* 1877, ii. 660.
[3] Widman, *Ber. Deutsch. Chem. Ges.* xix. 418.
[4] Widman, *ibid.* xix. 2773.

heated with potassium cyanide, and is a liquid which has a characteristic aromatic odour and boils at 260°—263°. The acid crystallizes from hot water in small needles, which melt at 158° and readily sublime.[1]

KETONES AND KETONIC ACIDS.

2496 a-*Durylmethylketone*, $(CH_3)_4C_6H.CO.CH_3$, is formed by the action of aluminium chloride on a mixture of *a*-tetramethylbenzene and acetyl chloride. It is a strongly refractive liquid, which has a characteristic, not unpleasant smell and boils at 253°—255°. It is reduced in alcoholic solution by zinc dust to a-*durylmethylcarbinol*, $(CH_3)_4C_6H.CH(OH)CH_3$, which is a yellowish liquid, boiling above 300°.

a-*Durylglyoxylic acid*, $(CH_3)_4C_6H.CO.CO_2H$, is obtained by careful oxidation of the ketone with potassium permanganate, as a light yellow, oily liquid, which forms crystalline salts and is reduced in alcoholic solution by sodium amalgam with formation of a-*durylhydroxyacetic acid*, $(CH_3)_4.C_6H.CH(OH).CO_2H$. This substance is only slightly soluble in water, readily in alcohol, crystallizes in short, rectangular prisms and melts at 156°. All these compounds are converted by the further action of potassium permanganate into a-*tetramethylbenzoic acid*, $(CH_3)_4C_6H.CO_2H$, which has hitherto only been obtained in the form of an oily liquid.

s-*Durylmethylketone* crystallizes in nacreous plates, melts at 63° and boils at 251°. On reduction it yields s-*durylmethylcarbinol*, which forms small, white plates, melting at 72°.

s-*Durylglyoxylic acid* crystallizes from alcohol in nacreous scales, which melt at 124°. It is converted by reduction with sodium amalgam and water into s-*durylhydroxyacetic acid*, which crystallizes in small, warty masses, melting at 146°. This is converted by oxidation into s-*tetramethylbenzoic acid*, which crystallizes in silver lustrous plates and melts at 109°.[2]

Methylbenzylaceto-acetic acid, $CH_3.CO.C(CH_3)(CH_2.C_6H_5)CO_2H$, is only known as the ethyl ether, which is obtained by the action of sodium ethylate and methyl iodide on benzylaceto-

[1] Kreysler, *Ber. Deutsch. Chem. Ges.* xviii. 1709.
[2] Claus and Foecking, *ibid.* xx. 3097.

acetic ether, as well as by that of benzyl chloride on sodium methylaceto-acetic ether. It is an aromatic smelling liquid, which boils at 287° and is converted into methylbenzylacetic acid by heating with concentrated caustic potash solution.[1]

Acetophenone-acetonecarboxylic acid, $C_6H_5.CO.CH_2.CH(CO.CH_3)CO_2H$. The ethyl ether of this acid is formed by the action of benzoylmethyl bromide, $C_6H_5.CO.CH_2Br$, on sodium aceto-acetic ether, and is an oily liquid, which decomposes on distillation. Dilute caustic potash solution readily saponifies it and the free acid is then precipitated by the addition of dilute sulphuric acid to the product. It forms crystals, but is extremely unstable and readily decomposes into acetophenone-acetone and carbon dioxide. If the ether be brought into hot alcoholic caustic potash, *dehydro-acetophenone-acetonecarboxylic acid*, $C_{12}H_{10}O_3$, is formed. This substance is precipitated by petroleum-ether from its solution in benzene in large crystals, melting at 113°—114°. It forms a hydroxylamine derivative and combines with phenylhydrazine. On boiling with hydrochloric acid for a short time, it is converted into the isomeric *phenylmethylfurfuric acid*, which crystallizes in white needles, melts at 180°—181° and readily sublimes. It does not combine with phenylhydrazine and is converted by continued boiling with acids or by heating to 240°—250° with water, into phenylmethylfurfuran.[2]

Its formation from dehydro-acetophenone-acetonecarboxylic acid may be explained in the following manner:

$$\begin{array}{l} CH_3.CO.CH.CO_2H \\ \quad\quad | \\ C_6H_5.C{\equiv}C \end{array} + H_2O = \begin{array}{l} CH_3.CO{-}{-}{-}CH.CO_2H \\ \quad\quad\quad\quad | \\ C_6H_5.C(OH){=}CH \end{array} =$$

$$\begin{array}{l} CH_3.C{=}C.CO_2H \\ O< \quad | \\ C_6H_5.C{=}CH \end{array} + H_2O.$$

Phenylmethylpyrrolcarboxylic acid, $C_{12}H_{11}NO_2$. The ethyl ether of this acid is formed when ethyl acetophenone-acetonecarboxylate is treated with aqueous ammonia:

$$\begin{array}{l} C_2H_5.CO_2.CH.CO.CH_3 \\ \quad\quad | \\ CH_2{=}CO.C_6H_5 \end{array} + NH_3 = \begin{array}{l} C_2H_5.CO_2.C{=}C.CH_3 \\ \quad\quad\quad\quad | \quad >NH \\ \quad\quad\quad\quad HC{=}C.C_6H_5 \end{array} + H_2O.$$

[1] Conrad and Bischoff, *Ann. Chem. Pharm.* cciv. 177.
[2] Paal, *Ber. Deutsch. Chem. Ges.* xvi. 2865; xvii. 913, 2756.

It crystallizes from alcohol in small tablets, which melt at 120°. The free acid forms long, flat, yellowish needles, which sublime on heating, a portion being simultaneously carbonized.

Derivatives in which the hydrogen of the imido-group is replaced are obtained by the action of amines or amido-bases on acetophenone-acetocarboxylic ether.[1]

DIBASIC ACIDS.

2497 *Orthophenylenedipropionic acid*, $C_6H_4(CH_2.CH_2.CO_2H)_2$. When ethyl chloromalonate is heated with sodium ethylate and orthoxylylene bromide in ethereal solution, the ethyl ether of *orthoxylylenedichlorodimalonic acid* is formed:

$$C_6H_4\begin{matrix}CH_2Br\\CH_2Br\end{matrix} + 2NaCCl(CO_2.C_2H_5)_2 =$$

$$C_6H_4\begin{matrix}CH_2.CCl(CO_2.C_2H_5)_2\\CH_2.CCl(CO_2.C_2H_5)_2\end{matrix} + 2NaBr.$$

It forms a thick syrup, which solidifies after standing for some time in long crystals and is converted by the action of zinc and glacial acetic acid into the ether of *orthoxylylenedimalonic acid*, an oily liquid, which decomposes on boiling with alcoholic potash into carbon dioxide, alcohol and orthophenylenedipropionic acid:

$$C_6H_4\begin{matrix}CH_2.CH(CO_2.C_2H_5)_2\\CH_2.CH(CO_2.C_2H_5)_2\end{matrix} + 6KOH =$$

$$2K_2CO_3 + 4C_2H_5.OH + C_6H_4\begin{matrix}CH_2.CH_2.CO_2K\\CH_2.CH_2.CO_2K\end{matrix}.$$

The free acid crystallizes from hot water in microscopic needles, which melt at about 160°—162°.[2]

[1] Lederer and Paal, *Ber. Deutsch. Chem. Ges.* xviii. 2591.

[2] Baeyer and Perkin, *ibid.* xvii. 452; Perkin, *ibid.* xix. 435; *Journ. Chem. Soc.* 1888, i. 14.

Metaphenylenedipropionic acid. When the reaction mentioned above is applied to metaxylylene bromide, the ethyl ether of *metaxylylenedichlorodimalonic acid* is obtained as a thick yellow liquid, which is converted by the action of zinc dust and acetic acid into *metaxylylenedimalonic ether.* This substance is also a liquid and yields the acid on boiling with a solution of caustic potash in methyl alcohol. The latter is an oily liquid and decomposes when heated alone, or more completely with water under pressure, into carbon dioxide and metaphenylenedipropionic acid, which crystallizes from hot water in splendid, lustrous tablets and melts at 146°—147°.

Paraphenylenedipropionic acid. In order to obtain this body, the ethyl ether of paraxylylenedichlorodimalonic acid is prepared. It crystallizes from alcohol in large, six-sided tablets, which melt at 86°—87°, and is converted by reduction into *ethyl paraxylylenedimalonate,* a crystalline substance, melting at 51°. The free acid separates out as a crystalline powder when its aqueous solution is evaporated and decomposes in a similar manner to the meta-compound when heated, paraphenylenedipropionic acid being formed. The latter is almost insoluble in water and separates from hot methyl alcohol in characteristic, knotted masses, which melt at 223°—224° and sublime without decomposition at a higher temperature.[1]

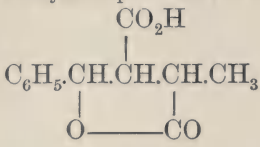
Phenylhomoparaconic acid, $C_{12}H_{12}O_4$, is formed in a similar manner to phenylparaconic acid by heating benzaldehyde with sodium pyrotartarate and acetic anhydride. It crystallizes from hot water in plates and separates from dilute alcohol in well-formed crystals, which melt at 177°. It yields two series of salts, like other similar lactonic acids. Those which contain two atoms of metal are derived from *phenylhomo-itamalic acid,* $C_6H_5.CH(OH)CH(CO_2H)CH(CH_3)CO_2H$, which is unknown in the free state. When phenylhomoparaconic acid is heated above its melting-point, it decomposes into carbon dioxide and phenyl-β-butylene (p. 327).[2]

In addition to this substance, the isomeric *phenylisohomoparaconic acid* is formed, a larger quantity being obtained when the foregoing mixture is only heated to 100°. It also crystallizes well and behaves in a similar manner to the preceding compound, but melts at 124·5°.[3]

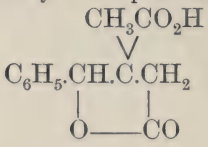
[1] Kipping, *Journ. Chem. Soc.* 1888, i. 21.
[2] Fittig, *Ann. Chem. Pharm.* ccxvi. 119.
[3] Fittig and Liebmann, *Ber. Deutsch. Chem. Ges.* xx. 3182.

The constitution of these acids is explained by the following formulæ:

Phenylhomoparaconic acid.

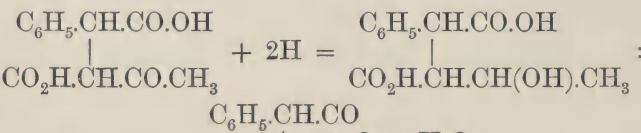


Phenylisohomoparaconic acid.



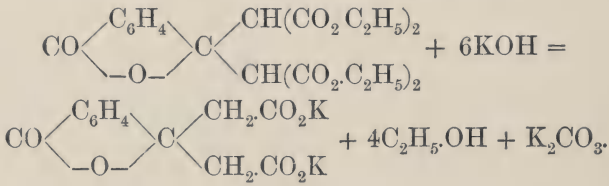
Phenylacetosuccinic acid, $C_6H_5.CH(CO_2H)CH(CO.CH_3).CO_2H$. The ethyl ether is formed by the action of ethyl phenylbromacetate, $C_6H_5.CHBr.CO_2.C_2H_5$, on sodaceto-acetic ether.[1] It crystallizes from dilute alcohol in small, lustrous plates, melting at 75°—76°. The free acid forms fascicular groups of large plates and melts at 120°—121°.

When the ether is treated in alcoholic solution with sodium amalgam, *phenylvalerolactonecarboxylic acid* is formed:



This crystallizes from dilute alcohol in quadratic plates, melting at 167·5°, and, like all lactonic acids, forms two series of salts.[2]

Phthalyldi-acetic acid, $C_{12}H_{10}O_6$. Phthalyldimalonic ether is always formed as a by-product in the preparation of phthalylmalonic ether. It crystallizes from alcohol in lustrous prisms, melting at 48·5°, and yields the potassium salt of phthalyldiacetic acid on boiling with caustic potash solution:



Phthalyldi-acetic acid is readily soluble in water and crystallizes from ether in vitreous prisms, which melt at 158°.[3]

[1] Rügheimer, *Ber. Deutsch. Chem. Ges.* xiv. 430.
[2] Weltner, *ibid.* lxvi. 18, 790.
[3] Wislicenus, *Ann. Chem. Pharm.* ccxlii. 23.

HYDROCARBONS, $C_{12}H_{16}$, AND THEIR DERIVATIVES.

2498 *Allylisopropylbenzene* or *Isopropylphenylpropylene*, $(CH_3)_2CH.C_6H_4.CH{=}CH.CH_3$, is formed when cumenylcrotonic acid is heated. A better yield is obtained by first preparing cumenylbromobutyric acid from it by the addition of hydrobromic acid and then heating this with sodium carbonate solution. It is a liquid, which boils at 229°—230° and does not polymerize when heated to 160°—200° for a considerable time. Its dibromide crystallizes from alcohol in tablets which melt at 59°.[1]

Phenylisohexylene, $C_6H_5.CH{=}CH.CH_2.CH(CH_3)_2$. When isohexylbenzene is treated with bromine vapour at 150° and the product distilled, this olefine is formed as the dibromide, $C_6H_5CHBr.CHBr.CH_2.CH(CH_3)_2$, which crystallizes from alcohol in small plates or needles, melting at 79°—80° (Schramm).

ACIDS OF THE FORMULA $C_{12}H_{14}O_2$.

2499 *Cumenylacrylic acid*, $(CH_3)_2CH.C_6H_4CH{=}CH.CO_2H$, was prepared by Perkin from cuminaldehyde by heating with sodium acetate and acetic anhydride.[2] It crystallizes from alcohol in white needles and from benzene in obliquely pointed prisms,[3] which melt at 157°—158°.

Orthonitrocumenylacrylic acid or *Orthonitro-isopropylcinnamic acid*, $(CH_3)_2CH.C_6H_3(NO_2)C_2H_2.CO_2H$, is formed by the action of fuming nitric acid on cumenylacrylic acid. Orthonitropropylcinnamic acid is simultaneously formed, the isopropyl being converted into the propyl group (Widman). Paranitrocinnamic acid is also present among the products, the isopropyl group having been by a remarkable reaction replaced by the nitroxyl group (Einhorn and Hess).

Nitrocumenylacrylic acid crystallizes from hot alcohol in hard, compact, straw-yellow prisms, which melt at 152°—153°. It is oxidized by chromic acid to orthonitrocumic acid. It com-

[1] Perkin, *Journ. Chem. Soc.* 1877, ii. 664.
[2] *Ibid.* 1877, i. 396 ; Einhorn and Hess, *Ber. Deutsch. Chem. Ges.* xvii. 2015.
[3] Widman, *ibid.* xix. 255.

bines with bromine to form *nitrocumenyldibromopropionic acid*, $(CH_3)_2CH.C_6H_3(NO_2)C_2H_2Br_2.CO_2H$, which crystallizes in monosymmetric prisms. If it be dissolved in caustic soda solution, the liquid boiled for a moment and a few grains of grape sugar added, cumine-indigo separates out.

Orthamidocumenylacrylic acid, $(CH_3)_2CH.C_6H_3(NH_2)C_2H_2.CO_2H$, is formed when ferrous sulphate solution is added to the ammoniacal solution of the nitro-acid. It crystallizes from alcohol in flat, strongly lustrous, yellow prisms, which melt at 165° with evolution of gas. When its hydrochloride is boiled with water, the following compound is formed.

Cumostyril, $(CH_3)_2CH.C_6H_3\begin{cases}CH=CH\\ |\\ N=C(OH)\end{cases}$, crystallizes from alcohol in long, lustrous needles, melting at 168°—169°.

Orthohydroxycumenylacrylic acid, $(CH_3)_2CH.C_6H_3(OH)C_2H_2.CO_2H$, is formed by the action of nitrous acid on the amido-acid and crystallizes from dilute alcohol in oblique needles, melting at 176°.

Metanitrocumenylacrylic acid is formed by heating metanitrocuminol with sodium acetate and acetic anhydride. It is very readily soluble in alcohol and crystallizes from hot benzene in transparent, obtuse-angled tablets, which melt at 141°.

Metamidocumenylacrylic acid crystallizes from ether in transparent, lustrous, six-sided tablets and melts at 165°.

Metahydroxycumenylacrylic acid crystallizes from alcohol in concentrically grouped flat needles or plates, melting at 205°—206°.

Orthonitropropylcinnamic acid, $C_3H_7.C_6H_3(NO_2)C_2H_2.CO_2H$, is readily soluble in hot alcohol and benzene and crystallizes from the latter in spherical aggregates of yellowish-white needles, which melt at 122°—123°. It is converted into orthonitroparapropylbenzoic acid by oxidation.

Orthamidopropylcinnamic acid, $C_3H_7.C_6H_3(NH_2)C_2H_2.CO_2H$, crystallizes from alcohol in yellow, lustrous needles, which melt at 154°—155°.[1] If it be treated in alcoholic solution with sodium amalgam, propylhydrocarbostyril is formed. This substance is also obtained in a similar manner from amidocumenylacrylic acid, the isopropyl being converted into the propyl group.[2] The same intermolecular change occurs when cumenylacrylic acid is converted into cumenylpropionic acid, since the acrylic

[1] Widman, *Ber. Deutsch. Chem. Ges.* xix. 273. [2] *Ibid.* xix. 413.

residue, like the methyl group, favours the formation of normal propyl derivatives.[1]

Isopropylcoumarin, $C_6H_4\begin{cases}CH{=}C.CH(CH_3)_2\\ O{-}{-}CO\end{cases}$, was obtained by Perkin, who named it "valeric coumarin," by heating sodium salicylaldehyde with valerianic anhydride. It crystallizes from alcohol in large, transparent prisms, which melt at 54° and have a faint odour, resembling that of coumarin.[2]

UNSATURATED DIBASIC ACIDS.

2500 *Phthalylaceto-acetic acid*, $C_{12}H_8O_5$, is only known in the form of the ethyl ether, which is obtained by the action of phthalyl chloride on sodium aceto-acetic ether:

$$C_6H_4\begin{cases}CCl_2\\ CO\end{cases}O + \begin{matrix}CH_2.CO.CH_3\\ |\\ CO_2.C_2H_5\end{matrix} =$$

$$C_6H_4\begin{cases}C{=}C.CO.CH_3\\ CO\end{cases}O \begin{matrix}\\ |\\ CO_2.C_2H_5\end{matrix} + 2HCl.$$

It crystallizes from hot alcohol or glacial acetic acid in six-sided plates; when it is gradually deposited, however, it forms compact, obtuse-angled crystals, melting at 124°.[3] It dissolves in cold concentrated sulphuric and nitric acids and is reprecipitated by the addition of water. When its solution in sulphuric acid is heated to 65°, it decomposes into alcohol, acetic acid and phthalylacetic acid. Cold ammonia converts it into phthalyldiamide. It combines with phenylhydrazine to form the compound $C_8H_4O_2 : C(CO_2.C_2H_5)C(CH_3)N_2H.C_6H_5$, which crystallizes in compact tablets and melts at 236°—238°.

Benzaceto-acetic-ether-orthocarboxylic acid, $CH_3.CO.CH(CO_2.C_2H_5)CH_2.C_6H_4.CO_2H$, is formed by the action of zinc dust and glacial acetic acid on the ether of phthalylacetic acid. It crystallizes in fascicular groups of needles, melts at 92° and is

[1] *Ber. Deutsch. Chem. Ges.* xix. 2796.
[2] Perkin, *Journ. Chem. Soc.* 1868, 58.
[3] E. Fischer and Koch, *Ber. Deutsch. Chem. Ges.* xvi. 651; Bülow, *Ann. Chem. Pharm.* ccxxxvi. 184.

converted by boiling with baryta water into benzylacetone-orthocarboxylic acid (p. 359). It combines with phenylhydrazine to form the compound $CH_3C(N_2H.C_6H_5)CH(CO_2.C_2H_5)CH_2.C_6H_4.CO_2H$, which crystallizes in yellowish needles and melts at 235° with decomposition (Bülow).

Phenyldehydrohexonecarboxylic acid, $C_{12}H_{12}O_3$. The ethyl ether is obtained by the action of trimethylene bromide and a solution of sodium in absolute alcohol on ethyl benzoylacetate:

$$\begin{array}{l} CH_2Br \\ | \\ CH_2.CH_2Br \end{array} + \begin{array}{l} O{=}C.C_6H_5 \\ | \\ CH_2.CO_2.C_2H_5 \end{array} = \begin{array}{l} CH_2{-}O{-}C.C_6H_5 \\ | \quad\quad \| \\ CH_2.CH_2.C.CO_2.C_2H_5 \end{array} + 2HBr.$$

It crystallizes from ether or petroleum-spirit in splendid monosymmetric prisms, melts at 59°—60° and boils at a higher temperature without decomposition. The free acid is only slightly soluble in water, readily in alcohol, from which it crystallizes in large, monosymmetric prisms. It melts at 142°—144° with evolution of carbon dioxide and decomposes completely at a slightly higher temperature into this and *phenyldehydrohexone*, $C_{11}H_{12}O$. This substance is a thick, aromatic smelling liquid, which boils at 249°—251° and polymerizes to a gelatinous mass on standing. It combines with hydrobromic acid to form benzoylbutyl bromide:

$$\begin{array}{l} C_6H_5.C{-}{-}O{-}{-}CH_2 \\ \quad\quad \| \quad\quad\quad | \\ \quad\quad CH{-}CH_2{-}CH_2 \end{array} + HBr = \begin{array}{l} C_6H_5.CO \\ | \\ CH_2.CH_2.CH_2.CH_2Br. \end{array}$$

The latter crystallizes from dilute alcohol in plates resembling those of benzoic acid, while it separates from petroleum-ether in oblique, six-sided tablets. Phenyldehydrohexone is regenerated when it is heated with alcoholic potash.

If the acid be boiled for some time with water, *benzoylbutyl alcohol*, $C_6H_5.CO.C_4H_8.OH$, is formed. It is a crystalline substance, which soon passes into its ether anhydride, phenyldehydrohexone.[1]

Benzal-lævulinic acid, $C_6H_5.CH{=}C(CH_2.CO.CH_3).CO_2H$, is formed when lævulinic acid is heated with benzaldehyde and

[1] Perkin, *Journ. Chem. Soc.* 1887, i. 726; *Ber. Deutsch. Chem. Ges.* xix. 2557.

sodium acetate, and forms small, compact crystals, which melt at 120°—125°. It is converted by alkaline reduction into *benzyl-hydroxypentylic acid*, $C_6H_5.CH_2.CH[CH_2.CH(OH).CH_3]CO_2H$, which is precipitated by acids in the form of its lactone. The latter crystallizes from carbon disulphide in large, transparent, colourless prisms, melting at 85°.[1]

HYDROCARBONS, C_nH_{2n-10}, AND THEIR DERIVATIVES.

2501 *Isobutenylstyrolene*, $C_6H_5.CH=CH.C=C(CH_3)_2$, was obtained by Perkin by heating cinnamaldehyde with isobutyric anhydride and sodium isobutyrate. It is a strongly refractive liquid, which boils at 245°—248°, has an aromatic odour and rapidly oxidizes in the air. A small quantity exposed to the air on a watch-glass becomes converted into a thick mass, resembling Canada balsam, within twelve hours.[2]

Cinnamenylcrotonic acid, $C_6H_5.CH=CH.CH=C(CH_3)CO_2H$, was prepared by Perkin from cinnamaldehyde by heating it with sodium propionate and propionic anhydride. It is readily soluble in alcohol, with difficulty in hot petroleum-spirit, from which it crystallizes in oblique, flat, transparent crystals, which melt at 157°—158° and become opaque when kept for some time.[3]

Phenylbutinedicarboxylic acid, $C_6H_5.CH=CH.CH=C(CO_2H)_2$ is formed when cinnamaldehyde is heated with malonic acid and glacial acetic acid. It crystallizes in yellow needles, which melt at 208° with evolution of gas and decompose completely at 210° into carbon dioxide and cinnamenylacrylic acid (p. 369), while, like benzalmalonic acid, it is unaffected by boiling with water.[4]

[1] Erdmann, *Ber. Deutsch. Chem. Ges.* xviii. 3441.
[2] *Journ. Chem. Soc.* 1879, i. 141.
[3] *Ibid.* 1877, 406.
[4] Stuart, *ibid.* 1886, i. 365.

COMPOUNDS CONTAINING MORE THAN TWELVE ATOMS OF CARBON.

Hydrocarbons, C_nH_{2n-6}, and their Derivatives.

2502 *Trimethyldiethylbenzene*, $C_6H(CH_3)_3(C_2H_5)_2$, is not known in the free state. Its amido-compound, $C_6(NH_2)(CH_3)_3(C_2H_5)_2$, is obtained by heating diethylpseudocumidine to 260°—280° with ethyl iodide. It is an oily liquid, boiling at 286°—290°, and forms a hydrochloride, which is insoluble in cold, slightly soluble in hot water and readily in alcohol, from which it crystallizes in fascicular groups of needles.[1]

s-*Methyldipropylbenzene*, $C_6H_3(CH_3)(C_3H_7)_2$, was obtained by Jacobsen, accompanied by mesitylene and s-dimethylpropylbenzene, by the distillation of acetone and methylpropylketone with sulphuric acid. It is a liquid, which boils at 243°—248° and is oxidized by nitric acid to uvitic acid.[2]

Dipropylmetacresol, $CH_3.C_6H_2(OH)(C_3H_7)_2$, is formed, together with propylmetacresol, when metacresol is heated with propyl alcohol and magnesium chloride to 200°; its acetate is a liquid, which boils at 255°—260°.

Di-isopropylmetacresol is obtained in a similar manner as a liquid, boiling at 251°. Its acetate is also a liquid and boils at 255°—260°.[3]

Amylxylene, $C_6H_3(CH_3)_2C_5H_{11}$, was prepared by Fittig and Bigot, by the action of sodium on a mixture of amyl bromide and bromometaxylene. It is a pleasant smelling liquid, which boils at 232°—233°.[4]

Heptylbenzene, $C_6H_5.C_7H_{15}$, is formed when a mixture of benzene and heptidene chloride, $C_6H_{13}.CHCl_2$, is treated with a large quantity of aluminium chloride. The first product is diphenylheptane, $(C_6H_5)_2CH.C_6H_{13}$, which is then decomposed into benzene and heptylbenzene. The latter boils at 110° at a pressure of 10 mm.[5]

Tetra-ethylbenzene, $C_6H_2(C_2H_5)_4$, is obtained, together with hexethylbenzene, by heating ethyl bromide and benzene with

[1] Ruttan, *Ber. Deutsch. Chem. Ges.* xix. 2382.
[2] *Ibid.* viii. 1258.
[3] Mazzara, *ibid.* xvi. 792.
[4] *Ann. Chem. Pharm.* cxli. 168.
[5] Krafft and Auger, *Ber. Deutsch. Chem. Ges.* xix. 2987.

aluminium chloride. It is a faintly aromatic smelling liquid, which boils at 251° and is oxidized by potassium permanganate to prehnitic acid.

Bromotetra-ethylbenzene, $C_6HBr(C_2H_5)_4$, is a heavy liquid, boiling at 284°.

Dibromotetra-ethylbenzene, $C_6Br_2(C_2H_5)_4$, crystallizes in colourless prisms, which melt at 74·5°.

Dinitrotetra-ethylbenzene, $C_6(NO_2)_2(C_2H_5)_4$, forms yellowish, transparent, rhombic prisms and melts at 115°.

Tetra-ethylbenzenesulphonic acid, $C_6H(C_2H_5)_4SO_3H$, crystallizes in small plates or deliquescent needles and forms salts, which crystallize well.

Tetra-ethylbenzenesulphamide, $C_6H(C_2H_5)_4SO_2.NH_2$, crystallizes from dilute alcohol in large, compact, monosymmetric prisms, which melt at 104°—105°.[1]

Octylbenzene, $C_6H_5.C_8H_{17}$, is formed by the action of sodium on a mixture of bromobenzene and octyl bromide [2] or octyl chloride.[3] It is a pleasant smelling liquid, which has a sweetish, burning taste, boils at 262°—264° and has a sp. gr. of 0·852 at 14°. It solidifies at −7° to a crystalline mass and is oxidized by chromic acid to benzoic acid, carbon dioxide and water.

Chloroctylbenzene, $C_6H_4Cl.C_8H_{17}$, is obtained by the action of chlorine in presence of iodine on the hydrocarbon and is an oily liquid, which boils at 275°.

Bromoctylbenzene, $C_6H_4Br.C_8H_{17}$, boils at 290°.

Para-iodo-octylbenzene, $C_6H_4I.C_8H_{17}$, was obtained by Beran from paramido-octylbenzene by means of the diazo-reaction. It is a heavy, yellow oil, which has a faint aromatic odour, boils at 318°—320° and is oxidized by chromic acid to paranitrobenzoic acid.

Ahrens has obtained an iodo-octylbenzene by treating octylbenzene with iodine and mercuric oxide. It is a yellow liquid, solidifies at −4° becomes instantly coloured red in the light and decomposes completely on heating.

Orthonitro-octylbenzene, $C_6H_4(NO_2)C_8H_{17}$, is formed, together with its isomerides, by the action of fuming nitric acid on the hydrocarbon. It is a thick, yellow oil, which has an aromatic odour and decomposes on heating.

Metanitro-octylbenzene crystallizes from alcohol in long, thin,

[1] Galle, *Ber. Deutsch. Chem. Ges.* xix. 1744.
[2] v. Schweinitz, *ibid.* xix. 640.
[3] Ahrens, *ibid.* xix. 2717.

pliant needles, which have a faint odour, melt at 123°—124° and sublime readily. It is converted by potassium permanganate into metanitrobenzoic acid.

Paranitro-octylbenzene is only formed in small quantity and can readily be separated from the meta-compound by sublimation, since it is less volatile. It is thus obtained in lustrous, yellowish needles, which melt at 204° and yield paranitrobenzoic acid on oxidation.

Paramido-octylbenzene, $C_6H_4(NH_2)C_8H_{17}$, is obtained when octyl alcohol is heated to 270°—280° with zinc-chloride-aniline, and in small quantity when the alcohol is heated to 300° with aniline hydrochloride. It is an odourless, oily liquid, which boils at 310°—311° and solidifies at a low temperature in large plates, melting at about 19·5°. It forms characteristic salts, which crystallize well.

Octylbenzoic acid, $C_8H_{17}.C_6H_4.CO_2H$, was first prepared by Beran, who heated the formyl derivative of the amido-base with zinc dust and converted the nitril thus obtained into the acid by heating with alcoholic potash. The free acid is slightly soluble in hot water and crystallizes from alcohol in small plates or needles, melting at 139°.

Paramido-caprylbenzene, $C_6H_{13}(CH_3)CH.C_6H_4.NH_2$, is obtained from secondary octyl alcohol in a similar manner to amido-octylbenzene and is an odourless liquid, which boils at 290°—292°, does not solidify at −20° and forms well-defined salts.

It is converted by the diazo-reaction into *para-iodo-caprylbenzene*, $C_6H_{13}(CH_3)CH.C_6H_4I$, a yellow, oily liquid, which boils at 304°—305° and is oxidized by chromic acid to paranitrobenzoic acid.[1]

Octyltoluene, $C_8H_{17}.C_6H_4.CH_3$, is still unknown; its amido-derivative is prepared by heating octyl alcohol with zinc chloride orthotoluidine to 280°; it is an odourless liquid, boiling at 324°—326°.[2]

Di-amylbenzene, $C_6H_4[C_5H_5(CH_3)_2]_2$, is formed by the action of aluminium chloride on a mixture of benzene and amyl chloride. It is an aromatic smelling liquid, which boils at about 265°, tastes like turpentine and has a sp. gr. of 0·8868 at 0°.[3]

Hexethylbenzene, $C_6(C_2H_5)_6$, is obtained when a mixture of benzene and ethyl bromide is allowed to stand in contact

[1] Beran, *Ber. Deutsch. Chem. Ges.* xviii. 131.
[2] *Ibid.* xviii. 145.
[3] Austin, *Bull. Soc. Chim.* xxxii. 12.

with aluminium chloride; it crystallizes from alcohol in arborescent monosymmetric prisms, often three or four inches in length, which readily cleave parallel to the axis of length, melt at 126° and boil at 305°.[1]

Cetylbenzene, $C_6H_5.C_{16}H_{33}$, is the product of the action of sodium on a mixture of iodobenzene and cetyl iodide. It crystallizes well, melts at 27° and boils at 230° at a pressure of 15 mm.

Cetylphenol, $C_6H_4(OH).C_{16}H_{33}$. Fuming sulphuric acid converts cetylbenzene into the sulphonic acid. The slightly soluble sodium salt of this yields the phenol on fusion with caustic potash. It crystallizes well, has neither taste nor odour, melts at 77·5° and boils at a pressure of 16 mm. at 260°—261°.

Amidocetylbenzene, $C_6H_4(NH_2)C_{16}H_{33}$. Cetylbenzene is converted by nitration into *nitrocetylbenzene*, $C_6H_4(NO_2)C_{16}H_{33}$, which is a crystalline powder, melting at 35°—36°, and is converted by reduction into amidocetylbenzene. The latter crystallizes well, melts at 53° and boils at 254°—255° at a pressure of 14 mm.

Octodecatylbenzene, $C_6H_5.C_{18}H_{37}$, has been prepared from octodecatyl iodide in a similar manner and crystallizes from alcohol in small, silver lustrous plates, melting at 36°. It boils at 249° at a pressure of 15 mm. and solidifies in lustrous tablets.

Octodecatylphenol, $C_6H_4(OH)C_{18}H_{37}$, crystallizes from alcohol in large, lustrous plates, which melt at 64°.[2]

PIPITZAHOÏC ACID, $C_{15}H_{20}O_3$.

2503 The root known as "Raiz del Pipitzahuac" is employed in Mexico as an energetic aperient, which produces no unpleasant after effects. In the year 1855, Professor Rio de la Loza discovered that the active substance is deposited in the root in the form of golden-yellow prisms, while Dr. Schaffner, of San Luis Potosi, sent a small specimen in the same year to Liebig, who intrusted Weld with the investigation. This chemist determined the composition of the substance and gave it the name which

[1] Galle, *Ber. Deutsch. Chem. Ges.* xvi. 1744.
[2] Krafft and Steinmann, *ibid.* xix. 2982.

is still used.[1] In 1856, Schaffner discovered the plant, which belongs to the order of the Compositæ, and named it *Trixis pipitzahuac.* After his death his collection passed into the hands of his friend, Vigener, of Biebrich, who found in it a large amount of the root and drew attention to it again in 1884. At his request an investigation of pipitzahoïc acid was undertaken by Anschütz, who carried it out in conjunction with Leather;[2] the subject was also studied by Mylius.[3]

It was found that the substance is not a monobasic acid, as was supposed by Weld, but a hydroxyquinone, $C_6HO_2(OH)(C_nH_{2n+1})(C_nH_{2n-1})$, containing two side chains, the constitution of which is still unknown.

Pipitzahoïc acid crystallizes from dilute alcohol or benzene in small, golden-yellow plates and from ether in oblique, rhombic tablets, which melt at 102°—103°, readily sublime and volatilize with steam. Its alkaline solution has the colour of potassium permanganate, the original substance being thrown down by carbon dioxide. Reducing agents convert it into the colourless hydropipitzahoïc acid, $C_{15}H_{18}(OH)_3$, which rapidly oxidizes in the air.

Anilidopipitzahoïc acid, $C_{15}H_{18}O_2(OH)NH.C_6H_5$, is formed by the action of aniline on the solution of the acid and crystallizes in dark purple coloured, lustrous needles, which melt at 133° and are converted by heating with ammonia into *amidopipitzahoïc acid,* $C_{15}H_{18}O_2(OH)NH_2$. This substance crystallizes from alcohol in lustrous, brownish red needles, melts at 151° and forms a deep blue coloured solution in alkalis.

Hydroxypipitzahoïc acid, is obtained by treating the hot alcoholic solution of the anilido-acid with sulphuric acid. It crystallizes from ether or benzene in red plates, which melt at 138° and form a purple coloured solution in alkalis.

ALCOHOLS OF THE FORMULA $C_nH_{2n-6}O$.

2504 The following compounds are, according to their empirical formulæ, homologous with benzyl alcohol, and are therefore described here although their constitution is quite unknown.

[1] *Ann. Chem. Pharm.* xcv. 88.
[2] *Ber. Deutsch. Chem. Ges.* xviii. 709 and 715; *Ann. Chem. Pharm.* ccxxxvii. 90.
[3] *Ber. Deutsch. Chem. Ges.* xviii. 936.

Cynanchol, $C_{15}H_{24}O$. *Cynanchum acutum*, a creeping plant, is looked upon in the district of the Oxus as exceedingly poisonous and especially harmful to camels. It contains a milky sap, which was investigated by Butlerow, who was unable to detect any poisonous principle in it. He obtained from it, however, a crystalline substance, to which he gave the name cynanchol.[1] Hesse has subsequently shown that it is a mixture of two compounds, which may be separated by recrystallization from alcohol.[2]

Cynanchin crystallizes in large, broad, lustrous plates, which melt at 148°—149° and are slightly soluble in cold, readily in hot alcohol.

Cynanchocerin forms lancet-shaped needles, melts at 145°—146° and dissolves readily in hot alcohol, while it is almost insoluble in cold alcohol.

Whether these compounds are really alcohols remains to be proved. They cannot be phenols, since they do not dissolve in alkalis, but may perhaps be ethers. Butlerow, to ascertain this, heated cynanchol with hydriodic acid and obtained a small amount of a volatile iodide, together with an amorphous residue, which was insoluble in alkalis. This result, therefore, favours the supposition that the substances are ethers.

Lactucerol or *Lactuceryl alcohol*, $C_{18}H_{30}O$. The poisonous lettuce (*Lactuca virosa*), contains a juice which, after drying, forms the German lactucarium, which is made in Zell, on the Moselle, where the plants are cultivated on the slopes.[3] It contains a large amount of a crystalline substance, which is called *lactucerin*. This substance was found by Hesse to be a mixture of the acetic ethers of two isomeric alcohols.[4] In order to prepare them, lactucarium is extracted with petroleum-ether, the solution evaporated and the residue exhausted with alcohol, which dissolves out the lactucerin. The latter is purified by recrystallization, saponified with alcoholic potash and the alcohols precipitated with water, washed and dried.

α-Lactucerol separates out on cooling when the mixture is boiled with a little alcohol, and is purified by boiling with animal charcoal and recrystallization. It crystallizes from alcohol of 90 per cent. in long, silky needles, which resemble those of caffeïne and contain one molecule of water, while it separates from ether or chloroform in anhydrous needles. It

[1] *Ann. Chem. Pharm.* clxxx. 352.
[2] *Ibid.* cxcii. 182.
[3] Flückiger, *Pharmakognosie*, 180.
[4] *Ann. Chem. Pharm.* ccxxxiv. 243.

melts at 179° and may be volatilized in a current of carbon dioxide. Its solutions are dextrorotatory.

α-Lactuceryl acetate, $C_{18}H_{29}.C_2H_3O_2$, is obtained by heating the alcohol with acetic anhydride; it crystallizes from hot alcohol in small plates and melts at 210°.

β-Lactucerol does not readily crystallize from alcoholic solution, but separates from ether or chloroform in long, silvery needles. Its solutions have a feebler rotatory power than those of the *α*-compound.

β-Lactuceryl acetate crystallizes in small plates, melting at 230°.

Sycoceryl alcohol, $C_{18}H_{30}O$. Among the products which were exhibited at Paris in 1855 was a resin which had been obtained from *Ficus rubiginosa*, in New South Wales, and which it was proposed to apply to technical purposes. It was investigated by Warren de la Rue and H. Müller, who found in it, together with a resin and caoutchouc, a crystalline substance, which they proved to be the acetate of an alcohol, to which they gave the name sycoceryl alcohol (*σῦκον*, fig; *κηρός*, wax). The resinous constituent is readily soluble in cold alcohol; boiling alcohol extracts the acetate from the residue, and it is then saponified by a solution of sodium in absolute alcohol.

Sycoceryl alcohol crystallizes from hot alcohol in silky needles, resembling those of caffeïne, which form masses resembling wavellite. It melts at 90° and is converted by acetyl chloride into the acetate.

Sycoceryl acetate, $C_{18}H_{29}.C_2H_3O_2$, crystallizes from alcohol in small plates and from ether in six-sided tablets, which melt at 118°—120°. It only undergoes slight decomposition on distillation.

Sycoceryl benzoate, $C_{18}H_{29}.C_7H_5O_2$, is formed when the alcohol is heated with benzyl chloride, and crystallizes from benzene in prisms.[1]

Cinchol or *Cinchyl alcohol*, $C_{20}H_{34}O$. It has long been known that Peruvian bark contains a fat or wax in addition to quinine and other alkaloids. This substance was first carefully investigated by Hesse, who found that it contains a series of isomeric alcohols. All genuine barks derived from the various species of cinchona contain one of these, which has been named cinchol. In order to extract it, the bark is exhausted with petroleum-spirit, the solution evaporated and the residue recrystallized

[1] *Phil. Trans.* 1860, 43; *Jahresber. Chem.* 1861, 637.

from alcohol. The crude product is then heated with acetic anhydride and the acetate thus obtained purified by further recrystallization and finally decomposed with alcoholic potash.

Cinchol crystallizes from alcohol in long leaflets or broad plates containing one molecule of water, which is lost on warming or on standing over sulphuric acid. It melts at 139° and volatilizes, apparently without decomposition, when heated in a current of hydrogen.

Cinchyl acetate, $C_{20}H_{33}.C_2H_3O_2$, crystallizes from hot alcohol in small white needles, melting at 124°. Its solution in chloroform, like that of cinchol itself, is lævorotatory.

Cupreol or *Cupreyl alcohol*, $C_{20}H_{34}O$, occurs with quinine in Cuprea bark (*Remijia pedunculata*, *R. Purdieana*) and with cinchol in several true cinchona barks, and is extracted in a similar manner to cinchol. It crystallizes from alcohol in satin-lustrous plates containing one molecule of water, and from petroleum-spirit in long, delicate needles, which melt at 140° and can be volatilized in a current of hydrogen. Its solution in chloroform is more strongly lævorotatory than that of cinchol.

Cupreyl acetate crystallizes from alcohol in small plates and melts at 126°.[1]

Quebrachol or *Quebrachyl alcohol*, $C_{20}H_{34}O$, occurs in the white Quebracho-bark (*Aspisdosperma Quebracho*), which also contains alkaloids and is employed in medicine in South America. Hesse has also detected it in some cinchona barks. It is obtained by extraction with petroleum-spirit and crystallization from alcohol. It crystallizes in small plates containing water, which is readily lost, melts at 125°, volatilizes without decomposition and has less lævorotatory power than cinchol.

Quebrachyl acetate forms small plates, which are anhydrous and melt at 115°.[2]

Ilicic alcohol, $C_{25}H_{44}O$, was discovered by Personne in bird lime, which is obtained by allowing the inner portion of the bark of the holly (*Ilex aquifolium*) to ferment. In order to prepare the alcohol, bird lime is dried at 100° and the residue extracted with chloroform and petroleum-spirit. This dissolves the ethereal salts of ilicyl, and these are then decomposed by heating with alcoholic potash. Ilicyl alcohol is scarcely soluble in dilute alcohol, readily in pure alcohol and forms nacreous crystals, which melt at 175° and volatilize at a higher temperature, forming a vapour, which has an aromatic odour.

[1] *Ann. Chem. Pharm.* ccxxviii. 288 ; ccxxxiv. 375. [2] *Ibid.* ccxi. 272.

Ilicic acetate, $C_{25}H_{43}.C_2H_3O$, forms crystals, which melt at 204°—206°.[1]

Mochyl alcohol, $C_{26}H_{46}O$, occurs as an ether of palmitic acid in *tori-mochi* or Japanese bird-lime, which is prepared from *Mochi-no-ki* (*Ilex integra*). It resembles ilicyl alcohol, melts at 234° and decomposes at a higher temperature with formation of *mochylene*, $C_{26}H_{44}$, which is a thick oil. In company with this substance occurs *ilicic alcohol*, $C_{22}H_{38}O$, which melts at 172°. Both of these alcohols are converted by heating with palmitic alcohol into a substance which is identical with purified bird-lime.[2]

HYDROCARBONS OF THE FORMULA C_nH_{2n-8}.

2505 *Isopropylbutenylbenzene* or *Isopropylphenylbutylene* $(CH_3)_2CH.C_6H_4.CH{=}CH.CH_2.CH_3$, was obtained by Perkin by combining cumenylangelic acid, prepared from cuminaldehyde, butyric anhydride and sodium acetate, with hydrobromic acid, and heating the product with sodium carbonate solution. It is a liquid, which boils at 242°—243°, has a sp. gr. of 0·8875 at 15° and has an odour, which resembles that of cuminaldehyde to a certain extent, but is fainter and more fruit-like.

Isopropylphenylbutenyl bromide, $C_{13}H_{18}Br_2$, crystallizes from alcohol in transparent tablets and melts at 77°.[3]

β-Isopropylbutenylbenzene or *Isopropylphenylisobutylene* $(CH_3)_2CH.C_6H_4.CH{=}C(CH_3)_2$, has been prepared by Perkin, who heated a mixture of isobutyric anhydride, cuminaldehyde and sodium isobutyrate. It boils at 234°—235°, has a sp. gr. of 0·889 at 15° and forms a liquid dibromide.[4]

ALCOHOLS OF THE FORMULA $C_nH_{2n-8}O$.

2506 These bodies, according to their empirical formulæ, are isomeric with cinnamyl alcohol; their constitution is still quite unknown.

Cholesterin or *Cholesteryl alcohol*, $C_{26}H_{43}.OH$. In the year 1788, Green drew attention to a characteristic fatty substance,

[1] J. and J. Personne, *Bull. Soc. Chim.* xlii. 150.
[2] Divers and Kawakita, *Journ. Chem. Soc.* 1888, i. 268.
[3] *Ibid.* 1877, ii. 665. [4] *Ibid.* 1879, i. 141.

which occurred in gall-stones. This body was classified by Fourcroy with spermaceti and adipocire (Pt. I. p. 677), but Chevreul pointed out the different nature of these bodies and named the substance in question cholesterin (*cholestérine, de χολὴ et στερεός, bile solide*).[1] It also occurs in the gall, brain, nerves, spleen, blood, milk and excrements, as well as in certain morbid products of the animal economy, in cod liver oil and other animal fats, and in fish, eggs, &c. It has also been discovered in Peru guano, and occurs in wool fat, partially in the free state and partially in the form of ethers. Berthelot has prepared several of its ethers and thus proved that it is an alcohol.[2] It is best obtained from gall-stones, which frequently consist almost entirely of it, by extracting the powder with boiling water and crystallizing the residue from alcohol. It may also be exhausted with benzene, the solution evaporated and the residue purified by recrystallization.[3]

If gall-stones are not obtainable, it may be extracted from the gall, which must be evaporated to a thin syrup and extracted with ether. Brains contain about 0·4 per cent. of cholesterin and 80 per cent. of water. If they be mixed with enough plaster of Paris to absorb all the water and the hard mass powdered and extracted with ether, the cholesterin and a small quantity of fat enter into solution. The liquid is then cooled to 0°, at which temperature the fat separates out, the filtered solution evaporated and the residue freed from adhering fat by boiling with alcoholic potash; it is then finally purified by recrystallization from alcohol.[4] Cholesterin crystallizes from chloroform in needles, which melt at 145°—146°, and from alcohol or ether in small plates or monosymmetric tablets, containing one molecule of water, which is lost over sulphuric acid or at 100°. It is insoluble in water, and is scarcely soluble in cold alcohol, but dissolves in hot alcohol, ether and chloroform. Its solutions are lævorotatory. It boils under diminished pressure above 360° (Chevreul), but may also be volatilized at the ordinary pressure, if it be carefully heated. It combines with bromine to form a dibromide, $C_{26}H_{44}Br_2O$, which crystallizes in thin needles.[5]

[1] *Recherches sur les Corps gras etc.* In the original, which contains a large number of printer's errors, the word is printed σερεὰ, instead of στερεός.
[2] Salkowski, *Zeitschr. anal. Chem.* xxvi. 557.
[3] Thudichum, *Frescnius' Zeitschr.* i. 122.
[4] Walitzky, *Beilstein's Handb.* ii. 678.
[5] Wislicenus and Moldenhauer, *Ann. Chem. Pharm.* cxlvi. 178.

Cholesterin gives several characteristic reactions. If it be brought into contact with sulphuric acid and a little iodine, a violet colouration is produced, which changes to blue, green and finally red. If its solution in chloroform be shaken with an equal volume of sulphuric acid of sp. gr. 1·76, the solution becomes coloured purple-red and the acid shows a green fluorescence. If a few drops of the chloroform solution be now poured into a basin, the colour changes into blue, green and finally yellow.[1] When cholesterin is evaporated with nitric acid, a yellow residue is left, which is coloured red when ammonia is added to it before it has cooled. The colour is not changed by caustic potash solution, so that cholesterin can in this way be distinguished from uric acid.[2]

In order to detect cholesterin, the suspected substance is heated with benzoic acid, the characteristic benzoate, which is described below, being formed.[3]

Cholesteryl chloride, $C_{26}H_{43}Cl$, is formed by the action of hydrochloric acid or phosphorous pentachloride on cholesterin and crystallizes from hot alcohol in long needles, which melt at 97°[4] and show a violet fluorescence.[5]

If it be heated with a solution of sodium in absolute alcohol, *cholesterylene*, $C_{26}H_{42}$, is formed. This body is only slightly soluble in alcohol, readily in ether and crystallizes in long transparent needles, melting at 80°.

When the chloride is boiled with alcohol and sodium amalgam, *hydrocholesterylene*, $C_{26}H_{44}$, is obtained. It forms feathery crystals, melting at 90°.[6]

Cholesteryl acetate, $C_{26}H_{43}.C_2H_3O_2$, is obtained by heating cholesterin with acetic acid, acetyl chloride or acetic anhydride (Rayman). It crystallizes from alcohol in small needles, melting at 113°.

Cholesteryl butyrate, $C_{26}H_{43}.C_4H_7O_2$, was obtained by Berthelot by heating cholesterin with butyric acid to 200°; it is a readily fusible mass.

Cholesteryl stearate, $C_{26}H_{43}.C_{18}H_{35}O_2$, crystallizes in small needles, melting at 65°.

[1] Hesse, *Ann. Chem. Pharm.* ccxi. 283; Salkowski, *Fresenius' Zeitschr.* xi. 443.
[2] Schiff, *ibid.* cxv. 313.
[3] Schulze, *Fresenius' Zeitschr.* xvii. 174.
[4] Berthelot, *Ann. Chim. Phys.* [3] lvi. 54; Löbisch, *Ber. Deutsch. Chem. Ges.* v. 510.
[5] Rayman, *Bull. Soc. Chim.* xlvii. 898.
[6] Walitzky, *Beilstein's Handb.* ii. 129 and 131.

Cholesteryl benzoate, $C_{26}H_{43}.C_7H_5O_2$, is scarcely soluble in boiling alcohol and crystallizes from ether in characteristic, rectangular tablets (Fig. 4), which melt at 150°—151°.

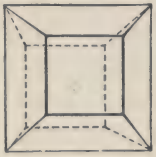


Fig. 4.

Cholesterylamine, $C_{26}H_{43}.NH_2$, is formed when the chloride is heated with alcoholic ammonia and crystallizes in small iridescent plates, which melt at 104° and then show a characteristic, bluish violet fluorescence, resembling that of the precious opal; this phenomenon is also shown by the fused chloride (Loebisch).

Dinitrocholesterin, $C_{26}H_{42}(NO_2)_2O$, is obtained by the action of fuming nitric acid on cholesterin and crystallizes from hot alcohol in fine needles, melting at 120°—121°.[1]

2507 *Isocholesterin*, $C_{26}H_{44}O$, occurs, together with cholesterin, in wool fat. The latter may be removed by extraction with alcohol, while its ethers and those of isocholesterin remain behind. The mixture is then saponified with alcoholic potash at 100° in closed vessels, the solution evaporated and the residue extracted with ether. Two isomeric alcohols are thus obtained in the ethereal solution, which is evaporated and the residue heated to 200° with four parts of benzoic acid. The benzoates thus obtained crystallize from ether in characteristic forms, which may be separated mechanically by washing and are then saponified.

Isocholesterin separates from a dilute alcoholic solution in plates, while its concentrated solution solidifies to a jelly. It crystallizes from ether or acetone in fine, transparent needles, melting at 137°—138°. It is dextrorotatory and gives the cholesterin reaction with chloroform.[2]

Its chloride and acetate are resinous; the stearate forms fine needles, melting at 72°.

Isocholesteryl benzoate crystallizes from ether in microscopic needles and from acetone in fascicular aggregates of lustrous needles, melting at 190°—191°.

[1] Preis and Raymann, *Ber. Deutsch. Chem. Ges.* xii. 224.
[2] Schulze, *Journ. Prakt. Chem.* [2] vii. 163; xxv. 458.

Phytosterin or *Phytosteryl alcohol*, $C_{26}H_{44}O$, was discovered by Benecke in leguminous fruits, almonds and other seeds, and was considered by him to be cholesterin,[1] until Hesse, who prepared it from Calabar beans, proved its individuality and gave it the name now in use[2] (*φυτόν*, plant). It is widely disseminated in the vegetable kingdom, and occurs in wheat, maize, cotton seed and probably all seeds, as well as in the fatty oils derived from them, in many fungi and in the sugar beet,[3] &c. It is best obtained from seed peas, which are extracted with petroleum spirit, the solution evaporated and the residue freed from an oily impurity by exposure on filter paper and then recrystallized from alcohol (Hesse).

It thus forms plates, containing one molecule of water, while it crystallizes from ether or chloroform in anhydrous needles melting at 132°—133°. It has a less rotatory power than cholesterin, but gives the same reaction with chloroform.[4] While cod-liver oil and other animal fats contain cholesterin alone, phytosterin always occurs in the oils derived from seeds, but is not contained in palm oil and only in small quantity in olive oil. An adulteration of cod-liver oil with seed oil can therefore be detected by isolating the cholesterin of the mixture. This substance when pure crystallizes from alcohol in characteristic tablets, melting at 146°, whilst the melting-point is lowered by the presence of phytosterin, and the needle-shaped crystals of the latter can readily be observed among those of cholesterin. Since olive oil only contains a very small quantity of phytosterin, while cotton-seed oil contains it in relatively large amount, an adulteration of the former with the latter may probably be recognized without much difficulty.[5]

Phytosteryl acetate, $C_{26}H_{43}.C_2H_3O_2$, crystallizes from hot alcohol in lustrous satiny plates, melting at 120°.[6]

Paracholesterin, $C_{26}H_{44}O$, is a constituent of *Aethalium septicum*, a fungus which grows on old tan heaps. It crystallizes from alcohol in plates, containing one molecule of water, and from ether or chloroform in silky needles, melting at 134°—135·5°.[7] It has a feebler lævorotation than phytosterin and gives the chloroform reaction (Schulze).

[1] *Ann. Chem. Pharm.* cxxii. 249.
[2] *Ibid.* cxcii. 175.
[3] Lippmann, *Ber. Deutsch. Chem. Ges.* xx. 3201.
[4] Hesse, *Ann. Chem. Pharm.* ccxi. 283.
[5] Salkowski, *Fresenius' Zeitschr.* xxvi. 557.
[6] Hesse, *Ann. Chem. Pharm.* ccxxviii. 296.
[7] Reinke and Rodewald, *ibid.* ccvii. 229.

Paracholesteryl benzoate, $C_{26}H_{43}.C_7H_5O_2$, crystallizes from ether in thin, lustrous, rectangular plates, which melt at 127°—128°.

Caulosterin, $C_{26}H_{44}O$, occurs in the root and stem (*caulis*, καυλός) of seedlings of the yellow lupine, which have been allowed to grow in the dark. It is also lævorotatory and gives the chloroform reaction; it crystallizes from alcohol in lustrous plates, containing a molecule of water of crystallization which is lost at 100°, and melts at 158°—159°. Its benzoate crystallizes from ether in thin lustrous plates.[1]

Daucosterin, $C_{26}H_{44}O$. A red colouring matter, which is known as *carotin*, occurs in the carrot (*Daucus carota*), together with a colourless body, termed *hydrocarotin* by Husemann in the belief that it only differed from carotin in containing a larger amount of hydrogen.[2] According to Arnaud, it is identical with phytosterin, but this view has been disputed by Reinitzer, who showed that it is a new cholesterin, for which he retained the name hydrocarotin.[3] The carrot contains about 0·01 per cent. of this substance, which crystallizes from acetone in long needles and from methyl alcohol in large, nacreous plates, containing water of crystallization, which is soon lost. It melts at 137°, is lævorotatory and gives the chloroform reaction. Its acetate forms scales, melting at 127·5°, while the benzoate crystallizes in tablets, which resemble those of cholesteryl benzoate and melt at 145°.[4]

[1] Schulze and Barbieri, *Journ. Prakt. Chem.* [2] xxv. 159.
[2] *Ann. Chem. Pharm.* cxvii. 200.
[3] *Compt. Rend.* cii. 1319.
[4] Reinitzer, *Monatsh. Chem.* vii. 597.

GROUP OF THE TERPENES AND CAMPHORS.

2508 The pines, firs, and other coniferous plants are rich in resins and volatile hydrocarbons. The resinous juice issuing from the bark of many of these trees or obtained from them by means of incisions, which is called turpentine and was known to the ancients, is a mixture of these. Dioscorides relates that the resin oil (*πισσέλαιον*) was extracted from this resin by boiling it with water in a vessel over which wool was suspended, which was allowed to become saturated with the vapours and then wrung out into another vessel. The same method is described by Pliny: *E pice fit, quod pissinum appellant, quum coquitur, velleribus supra halitum ejus expansis, atque ita expressis; . . . . color oleo fulvus.*

As the process of distillation was gradually improved, oil of turpentine was more frequently prepared and, like spirits of wine, received the name *aqua ardens.*

Marcus Graecus, who lived in the eighth century, or according to some authors at a later period, gives the following directions: *Recipe terebinthinam, et destilla per alambicum aquam ardentem, quam impones in vino cui applicatur candela et ardebit ipsa.* Libavius treats of it in an appendix to his chapter on alcohol, and it was rarely at that early period described as an oil, this word being however used by Arnoldus Villanovanus in the thirteenth century and in the fifteenth century by Johann von St. Amando, a physician of Tournay, who says: *Oleum de terebinthina fit similiter per sublimationem, et est clarum ut aqua fontis, et ardet ut ignis graecus.*

Libavius generally speaks of it as *spiritus terebinthinae*, and Lemery as *esprit de therebentine*, but the latter chemist remarked in 1700 that this spirit is really *une huile aetherée.*

Other volatile oils became known in the thirteenth century. Raymond Lully says that such are obtained by the distillation of

many plants with water and speaks more particularly, in common with Arnoldus Villanovanus, of oil of rosemary. A very large number of ethereal oils was then prepared by the adherents of Paracelsus in their endeavours to extract the quintessence from plants.

It was long believed that the characteristic odour of these oils did not arise from the oils themselves but from a substance mixed with them. This odorous body, which was thought to be extremely subtle and scarcely ponderable, was named *spiritus rector* by Boerhave in the year 1732. Macquer in 1778 expressed the opinion that it was a true gas, and Fourcroy in 1794 devoted an entire chapter of his *Elemens d'Histoire naturelle et de Chimie* to the discussion of this *arôme;* four years later, however, he sought to prove that the odour was that of the oils themselves and was not due to an admixed substance.

The investigation of these oils showed that many of them, as oil of turpentine, oil of lemons, &c., have the formula $C_{10}H_{16}$, and that isomeric hydrocarbons, frequently accompanied by other compounds, occur in other ethereal oils. These yield isomeric or polymeric hydrocarbons when submitted to the action of heat or sulphuric acid. It was further observed that oil of turpentine combines with hydrochloric acid to form a crystalline compound, $C_{10}H_{16}.HCl$, an isomeric liquid being simultaneously formed, while oil of lemons yields the solid body, $C_{10}H_{16}(ClH)_2$. Oil of turpentine also combines with water under certain conditions to form the crystallized hydrate $C_{10}H_{16} + 2H_2O$, which was also obtained from other ethereal oils.[1]

Berthelot, who made a detailed investigation of oil of turpentine and its derivatives, came to the following conclusions:

Oil of turpentine exists in two optically isomeric modifications, the lævorotatory *terebentene* and the dextrorotatory *australene* (p. 415). Both of these yield the isomeric hydrochlorides mentioned above, while a dihydrochloride is formed by the continued action of concentrated hydrochloric acid, which appears to be identical with that derived from oil of lemons. In addition to these, an unstable, liquid compound of the formula $C_{10}H_{16}(ClH)_2 + 2(C_{10}H_{16}.HCl)$ exists. Careful elimination of the hydrochloric acid from the solid monohydrochlorides yields the isomeric crystalline hydrocarbons *terecamphene* and *austracam-*

[1] Dumas, *Ann. Chem. Pharm.* vi. 245; Blanchet and Sell, *ibid.* vi. 259; Blanchet, *ibid.* vii. 154; Souberan and Capitaine, *ibid.* xxxiv. 311; Deville, *ibid.* xxxvii. 176; lxxi. 349; Wiggers, *ibid.* xxxiii. 358; lvii. 247; see also *ibid.* li. 390.

phene, which are also optically different, while an *inactive camphene* (p. 417) is formed under other conditions. These hydrocarbons form hydrochlorides from which they can be isolated unaltered. Oil of turpentine is converted by heating into *isoterebene* or *austraterebene*, which, like oil of lemons, combines with two molecules of hydrochloric acid and occupies an intermediate position between oil of turpentine and oil of lemons.

Berthelot then gives the following *résumé:*

"The hydrocarbon, $C_{10}H_{16}$, in certain of the forms in which it occurs in nature, as for example in terebentene, is the starting point for two series of compounds: (1) The monatomic camphol series (including the monohydrochloride or camphhol hydrochloric ether $C_{10}H_{17}Cl$, the camphenes, $C_{10}H_{16}$, and the camphol alcohols, $C_{10}H_{16}O$). (2) The diatomic terpil series (including the dihydrochlorides, the hydrates, $C_{10}H_{20}O_2$, and the terpilenes).

"Each of these series forms a chief group, which is divided into secondary series (australene, terebentene, &c.), the isomeric members of which correspond in pairs. Each of these series has an inactive hydrocarbon as type, that of the first group being camphene and of the second group terpilene."[1]

In addition to this, oil of turpentine is converted by the action of sulphuric or phosphoric acid into the inactive *terebene*, which combines with hydrochloric acid to form a semi-hydrochloride $(C_{10}H_{16})_2HCl$.

As it had been found that the isomeric hydrocarbons, $C_{10}H_{16}$, are closely related to camphor, they had been termed *camphenes*, but as this name was subsequently adopted by Berthelot for a single definite substance, it was changed to *terpenes*.[2] The close relations existing between these substances and cymene were not discovered till a later period. It was believed that an extremely large number of terpenes existed, which differed from each other in physical properties, such as optical behaviour, smell, boiling-point, &c., and that numerous chemical isomerides existed in addition to these physical isomerides.

Light was first thrown upon this little-understood group by the researches of Tilden. This chemist, in conjunction with Shenstone, found that the substances in question can be divided into two classes; the members of the first of which boil at about 160°, while the boiling-points of the second class approach

[1] *Ann. Chem. Pharm.* lxxxiv. 350; cx. 367; *Suppl.* ii. 226.
[2] Kekulé, *Lehrb.* ii. 464.

174°. Both combine with nitrosyl chloride to form compounds $C_{10}H_{16}NOCl$, which exhibit characteristic differences.[1] He subsequently showed that those of the first class, to which oil of turpentine belongs, form a solid monohydrochloride with hydrochloric acid and that the liquid product simultaneously formed is a mixture of cymene with monohydrochloride and a dihydrochloride. The latter is readily formed by the action of hydrochloric acid on the higher boiling terpenes, such as:

Citrene from oil of lemons,
Hesperidene from oil of oranges,
Bergamene from oil of bergamot,
Carvene from cumin oil,
Terpene from pine-needle oil,
Terpene from resin spirit.

Sylvestrene, a substance which occurs in Swedish and Russian oil of turpentine, also forms a characteristic dihydrochloride.[2] Riban had previously found that the terebene, which is formed by the action of concentrated sulphuric acid on oil of turpentine, is a mixture of cymene with a terpene, which he looked upon as pure terebene. Armstrong and Tilden, however, showed that the latter contains camphene and another terpene, for which they retained the name of *terpilene*;[3] it is also formed when terpene dihydrochloride is heated with water and when the hydrate is treated in a similar manner with dilute sulphuric acid.

A complete explanation of this subject was first given by Wallach's detailed investigation. According to this chemist, there are eight chemically different terpenes, which fall into three classes:

Pinene	Limonene	Terpinene
Camphene	Dipentene	Phellandrene
	Sylvestrene	
	Terpinolene	

Pinene, which exists in two optically isomeric forms, occurs in oil of turpentine and other ethereal oils. It forms a monohydrochloride, which is converted by elimination of hydrochloric

[1] *Journ. Chem. Soc.* xxxi. 554.
[2] *Ber. Deutsch. Chem. Ges.* xii. 1133.
[3] *Ibid.* xii. 1752.

acid into camphene. The latter combines with one molecule of hydrochloric acid and may be reobtained unaltered from this compound.

The terpenes of the second group are characterized by the formation of crystalline tetrabromides, $C_{10}H_{16}Br_4$, by means of which they can be readily detected. Pinene and limonene are converted by being strongly heated into dipentene, which forms the same dihydrochloride as is formed by the action of concentrated hydrochloric acid on pinene and of hydrochloric acid gas on limonene. The latter terpene occurs in several ethereal oils, while sylvestrene is a product of the dry distillation of pine-wood and is a very stable compound. Terpinolene and terpinene are constituents of terpilene and of the products of the further decomposition of dipentene. This substance, as also terpinene and phellandrene, is found in nature. The two latter are distinguished by the formation of crystallized compounds of the formula $C_{10}H_{16}N_2O_3$, with nitrogen trioxide.

The smell of the pure terpenes resembles that of oil of lemons or oranges in a greater or less degree.

THE PINENE GROUP.

2509 *Oil of turpentine* has been long prepared by the distillation of turpentine with water, that derived from *Pinus maritima* being employed for this purpose in South-west France. The French oil of turpentine consists almost entirely of lævo-pinene or terebentene, which also occurs in Strassburg turpentine (*Pinus picea*), in Venetian turpentine (*Pinus larix*) and in Canada balsam (*Pinus balsamea*). English oil of turpentine, so called because it comes to the European markets from England, is prepared in the United States, especially in North Carolina, from the turpentine of *Pinus australis*. It is simply distilled from copper retorts without the addition of water and the oil received in the casks in which it is exported.[2] It contains dextropinene or australene, which also occurs, together with sylvestrene, in Swedish and Russian oil of turpentine. The latter product differs from those already described in not being

[1] Flückiger and Hanbury, *Pharmacographia*, 2nd Edit. 605.

obtained from turpentine but from pine-wood tar (*Pinus sylvestris* and *Pinus Ledebourii*).

Another product, named templinol or oil of fir-cones, is prepared in Switzerland from the cones of the silver fir (*Pinus picea*).[1] It consists of lævopinene and has a very pleasant smell, resembling that of orange flowers, while the freshly prepared oil from the turpentine of the same tree has a smell resembling that of lemons.[2]

Commercial oil of turpentine contains oxidation products and has a characteristic, unpleasant smell; when heated to 250°—270°, it is partially polymerized and partially converted into the isomeric dipentene. If its vapour be passed through a tube heated to just below redness, isoprene, C_5H_8, heptine, C_7H_{12}, toluene, metaxylene, cymene, terpilene (dipentene) and polyterpenes are formed,[3] while the products at a red heat are benzene, toluene, metaxylene and its isomerides, naphthalene, phenanthrene, anthracene and methylanthracene, all of which occur in coal-tar.[4]

Chlorine acts so energetically on oil of turpentine as to cause ignition, so that when paper soaked in the oil is brought into chlorine gas, finely divided carbon separates out and hydrochloric acid is formed. Substitution products are formed by a more moderate action, or addition may take place, bromine acting in similar manner. When iodine is added to oil of turpentine, it dissolves and the mass then detonates, hydriodic acid being evolved; if it be very gradually added and the mixture heated, cymene is formed.

Oil of turpentine absorbs oxygen very readily, carbon dioxide, formic acid, acetic acid, &c., being formed and the whole being finally converted into a resinous mass. According to Schönbein, ozone is also formed in this gradual oxidation and combines with the oil of turpentine to form a characteristic, strongly oxidizing compound, while Kinzett states that the peroxide, $C_{10}H_{14}O_4$, is formed and that this decomposes on heating with water into hydrogen peroxide and camphoric acid.[5]

$$C_{10}H_{14}O_4 + 2H_2O = C_{10}H_{16}O_4 + H_2O_2.$$

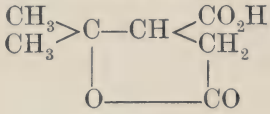
The ignition of oil of turpentine by the addition of fuming

[1] Flückiger, *Jahresb. Chem.* 1855, 642.
[2] Blanchet and Sell, *Ann. Chem. Pharm.* vi. 262.
[3] Tilden, *Journ. Chem. Soc.* xlv. 411.
[4] Schultz, *Ber. Deutsch. Chem. Ges.* x. 113.
[5] *Journ. Chem. Soc.* xvii. 511; xviii. 210; xix. 243.

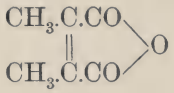
nitric acid was known in the seventeenth century, as was also the fact that other oils behave in a similar manner. Geoffroy in 1726 stated that the experiment succeeds most completely when a mixture of nitric and sulphuric acids is employed, and this was confirmed by Rouelli in 1747.

A series of products has been obtained by the action of dilute nitric acid on oil of turpentine, the constitutions of some of which have only been recently ascertained. Acetic, propionic, paratoluic and terephthalic acids are formed, together with terebinic acid, $C_7H_{10}O_4$, and dimethylfumaric anhydride,[1] $C_6H_6O_3$. The latter compounds have the following constitutional formulæ:

Terebinic acid.



Dimethylfumaric anhydride.



Chromic acid solution converts oil of turpentine into acetic acid, terebinic acid and terpenylic acid, $C_8H_{12}O_4$, the constitution of the last of which is still unknown, a small quantity of phthalic acid being also formed.[2]

A current of boron fluoride converts oil of turpentine into a polymeride, which is a viscid, fluorescent liquid and boils at 300° (Berthelot).

Since oil of turpentine readily dissolves resins, it is employed for the manufacture of lacs and varnishes and as a diluent of oil-colours. It is a strong antiseptic and is employed in medicine, its vapour being inhaled, for example, in cases of bronchitis, while the old oxidized oil serves as an antidote against phosphorus poisoning. When taken inwardly, it imparts the odour of violets to the urine, a fact which was known to the Romans; the same effect is produced when the body is exposed to its vapours for a considerable time.

2510 *Terebentene* or *Lævopinene*, $C_{10}H_{16}$, was obtained by Berthelot by neutralizing French oil of turpentine with sodium carbonate and distilling under diminished pressure. It also occurs in oil of thyme and in oil of anise (Brühl), boils at 156° and has a sp. gr. of 0·8767 at 0°.[3]

[1] Mielck, *Ann. Chem. Pharm.* clxxx. 45; Bredt, *ibid.* ccviii. 58; Roser, *Ber. Deutsch. Chem. Ges.* xv. 293, 1318 and 2381; Otto and Beckurts, *ibid.* xviii. 825; Frost, *Ann. Chem. Pharm.* ccxxvi. 368; Erdmann, *ibid.* ccxxviii. 176.

[2] Fittig and Krafft, *ibid.* ccviii. 74.

[3] Riban, *Ann. Chim. Phys.* vi. [5] 14.

Australene or *Dextropinene* has the same properties, but is dextrorotatory. It occurs in oil of turpentine, and also in those of wormwood and mint (*Mentha viridis*).

Nitropinene, $C_{10}H_{15}.NO_2$. Nitrous acid acts upon terebentene with formation of a green oil, which has not been prepared in a state of purity. It is converted by the action of ammonia into nitropinene, a yellow oil, which decomposes on heating.

Amidopinene, $C_{10}H_{15}.NH_2$, is formed by the reduction of nitropinene and is a light, colourless liquid, which boils at 197°—200°, and is converted by methyl iodide into *pinyltrimethylammonium iodide*, $C_{10}H_{15}N(CH_3)_3I$, which crystallizes in nacreous plates.

Pinene dichloride, $C_{10}H_{16}Cl_2$, is obtained when chlorine is passed into oil of turpentine at − 15°, and is a liquid, which decomposes on heating into hydrochloric acid and cymene, products which are also formed, together with a diterpene $C_{20}H_{32}$, when it is heated to 100° with zinc dust.[2]

Pinene dibromide, $C_{10}H_{16}Br_2$, is formed when bromine is added through a capillary tube to well-cooled oil of turpentine, and is a liquid which is converted into cymene by heating with anilin.[3]

Pinene nitrosochloride, $C_{10}H_{16}NOCl$, is obtained by passing nitrosyl chloride into a mixture of English or French oil of turpentine with chloroform, the liquid being cooled by a freezing mixture of salt and ice. It is a snow-white, crystalline powder, which is converted by alcoholic caustic soda into *isonitrosopinene* or *pinoxime*, $C_{10}H_{14}(N.OH)$. This substance crystallizes from hot alcohol in transparent, monoclinic prisms, melts at 129°, readily sublimes and is only slightly soluble in water, but readily in hot caustic soda solution.[4]

Its ethereal solution yields with sodium ethylate a precipitate of $C_{10}H_{14}(NONa)$, which is converted by heating with methyl iodide into the methyl ether, $C_{10}H_{14}(NOCH_3)$, a liquid which smells like carrots.[5]

Pinene hydrochloride or *Pinyl chloride*, $C_{10}H_{17}Cl$, was discovered by Kindt in 1803 and described as *artificial camphor*.[6]

This *hydrochloride of oil of turpentine* or *terpene monohydrochloride*, as it was subsequently called, is obtained by passing

[1] Pesci and Bettelli, *Gaz. Chim. Ital.* xvi. 337.
[2] Naudin, *Bull. Soc. Chim.* xxxvii. 111.
[3] Oppenheim, *Ber. Deutsch. Chem. Ges.* v. 628.
[4] Tilden, *Journ. Chem. Soc.* xxvii. 514; Maskelyne, *ibid.* xxvii. 518; Tilden and Shenstone, *ibid.* xxxi. 554.
[5] Goldschmidt and Zürrer, *Ber. Deutsch. Chem. Ges.* xviii. 2223.
[6] Trommsdorff's *Journ. Pharm.* xi. 2, 132.

hydrochloric acid into cooled oil of turpentine[1] diluted with carbon disulphide[2] or benzene;[3] according to Wallach, these diluents are superfluous, it being only necessary to avoid the presence of any trace of water and to prevent the temperature rising, as otherwise a certain amount of dipentene dihydrochloride is obtained and forms with the pinyl chloride a mixture, which has a very low freezing point.

Pinyl chloride is a crystalline mass, which appears and smells like camphor; it is deposited from alcoholic solution in feathery crystals, which possess the unpleasant property of welding to a viscous mass, which adheres firmly to all objects with which it comes into contact. It melts at 125°, boils at 210°, does not combine with dry hydrochloric acid or bromine and is not decomposed by silver nitrate in the cold.

Pinyl bromide, $C_{10}H_{17}Br$, was obtained by Deville by the action of hydrobromic acid on oil of turpentine.[4] It melts at 90°, resembles the chloride and boils with decomposition at a slightly higher temperature than this (Wallach).

2511 Pinenes also occur in the following ethereal oils, their presence being proved by converting the fraction which boils at about 160° into dipentene by heating or by preparing the tetrabromide from this (Wallach) or by preparing the nitrosochloride (Tilden and Shenstone).

Fir-wool oil is obtained in the preparation of fir wool, by boiling the needles of *Pinus sylvestris* with water and condensing the vapour. It has a pleasant odour of lavender,[5] and contains a pinene besides a large amount of limonene (Wallach). It finds application in medicine.

Oil of juniper is prepared both from the ripe and unripe berries; the latter has an odour resembling those of juniper and pine needles simultaneously. It is employed in medicine, and forms a constituent of gin (*Genièvre.*) The pinene, which can be isolated by fractional distillation, amounts to about one-third of the whole and is feebly lævorotatory.

Oil of sage, extracted from the leaves of *Salvia officinalis*, contains *salviol*, $C_{10}H_{16}O$, ordinary camphor and a pinene, which has all the properties of terebentene.[6]

[1] Oppermann, *Pogg. Ann.* xxii. 89.
[2] Berthelot, *Ann. Chim. Phys.* [3] xl. 5.
[3] Tilden, *Ber. Deutsch. Chem. Ges.* xii. 1131.
[4] *Ann. Chem. Pharm.* ccxxxix. 4.
[5] *Ann. Chim. Phys.* lxxv. 45, 54.
[6] Muir, *Journ. Chem. Soc.* xxxvii. 678; Muir and Sigiura, *ibid.* xxxiii. 292; Tilden and Shenstone, *loc. cit.*

Oil of rosemary. Rosemary (*ros marinus*) is mentioned even by Pliny and was well known to the Spanish-Arabian physicians, being highly prized throughout the Middle Ages. Charlemagne recommended the cultivation of this plant, which is indigenous to the coasts of the Mediterranean, and occurs in Africa as far inland as the Sahara, whence the dried plants are transported by caravans into Central Africa. The ethereal oil was distilled from it by Raymond Lully, and its extraction is fully described by Arnaldus Villanovanus in his tract *De Vinis.*

Oil of rosemary is manufactured in the south of France, Italy and Dalmatia. It is employed in pharmacy and perfumery and contains a pinene, accompanied by camphor, borneol, and cineol.[1]

Oil of Eucalyptus is obtained from the fresh leaves of *Eucalyptus globulus* and other species of eucalyptus. It has a characteristic aromatic odour and a burning, spicy taste producing a cooling after-effect. It is a strong antiseptic and is on this account employed in medicine. It contains one pinene, a terpene, which boils at 172°—175°, cymene,[2] and cineol.

Oil of mace is obtained from mace, the arillus or husk-like envelope of nutmeg, and like the ethereal oil extracted from the nutmeg itself, consists chiefly of a dextropinene.

CAMPHENE GROUP.

2512 *Camphene* or *Bornylene*, $C_{10}H_{16}$, exists in three optically isomeric but chemically identical modifications. Berthelot obtained the lævorotatory *terecamphene* by heating pinyl chloride or pinyl bromide, prepared from terebentene, with dry soap or potassium stearate to 200°—220°, while australene yielded the dextrorotatory *austracamphene.* An *inactive camphene*, however, was the chief product when sodium benzoate was substituted for the stearate.[3]

Riban found that terecamphene may be readily prepared by heating the hydrochloric acid compound of terebentene for some time to 180° with alcoholic potash, and that inactive camphene is formed when the same substance is heated to 170° with potassium

[1] Weber, *Ann. Chem. Pharm.* ccxxxviii. 90.
[2] Faust and Homeyer, *Ber. Deutsch. Chem. Ges.* vii. 63 and 1429.
[3] *Ann. Chem. Pharm. Suppl.* ii. 226.

acetate or sodium acetate. He also obtained *Borneo-camphene* by the action of alcoholic potash on bornyl chloride, a substance which will be subsequently described.[1] This compound may be more readily prepared by heating the chloride for twenty hours to 90°—95° with a large quantity of water and a little magnesia.[2] It is also formed by the action of sodium on an ethereal solution of the so-called camphor chloride (p. 429).[3] According to Riban, it is inactive, whilst Kachler states that it is dextrorotatory; if it be purified by conversion into the hydrochloric acid compound and again separated, it is found to possess a very faint dextrorotation (Kachler and Spitzer). Bouchardat and Lafont, who prepared camphene by heating the pinyl chloride, which is prepared from French oil of turpentine, with alcohol and potassium acetate, found that the rotation varies with the temperature employed and the duration of the preparation,[4] obviously because the lævorotatory modification is partially converted into the dextrorotatory; inactive camphene must therefore also be formed.

The oils of myrtle and rosemary probably contain a camphene in addition to pinene (Brühl).

In order to prepare camphene, bornyl chloride is warmed with an equal weight of aniline and the mixture then heated to the boiling-point of the latter. The reaction, accompanied by separation of aniline hydrochloride, occurs suddenly and is complete after a few minutes. The mass is then allowed to cool, treated with hydrochloric acid and the camphene distilled off with steam.[5]

It may also be readily obtained by heating equal parts of pinyl chloride and anhydrous sodium acetate to 200° for three or four hours with twice the weight of glacial acetic acid, or by simply heating a mixture of pinyl bromide and glacial acetic acid for some time in a flask connected with an inverted condenser.[6]

Camphene is also formed, accompanied by other products, by the action of concentrated sulphuric acid on oil of turpentine (p. 422) (Armstrong and Tilden).[7]

It forms a crystalline mass, resembling paraffin, which has,

[1] *Ann. Chim. Phys.* [5] vi. 353.
[2] Kachler, *Ann. Chem. Pharm.* cxcvii. 86.
[3] Kachler and Spitzer, *ibid.* cc. 340; Montgolfier, *Ann. Chim. Phys.* [5] xiv. 104.
[4] *Bull. Soc. Chim.* xlvii. 488.
[5] Wallach, *Ann. Chem. Pharm.* ccxxx. 233.
[6] *Ibid.* ccxxxix. 6.
[7] *Ber. Deutsch. Chem. Ges.* xii. 1752.

according to Riban, a characteristic stale smell, while according to other authorities its odour resembles those of turpentine and camphor. It separates from alcoholic solution in feathery crystals, melts at 51°—52°, boils at 160° and readily combines with hydrochloric acid to form bornyl chloride.

Monobromocamphene, $C_{10}H_{15}Br$, is formed when bromine is allowed to drop into a solution of camphene in a mixture of ether and alcohol. It is an oily liquid, which boils between 230°—240° with slight decomposition (Wallach).

2513 *Bornyl alcohol*, $C_{10}H_{17}.OH$. The history of this compound, which is usually termed *Borneo-camphor* or *borneol*, will be treated in connection with that of camphor. It occurs in the pith cavities of *Dryobalanops camphora*, a magnificent tree growing in Borneo, Sumatra and Labua, and is also found in *D. longifolia* and *D. Becarii*. In order to obtain borneol, the trees are felled and split and the camphor picked out. It is used to some extent on the spot as incense, especially in the observation of funeral rites, and is exported to China, Japan and other districts of Eastern Asia for similar purposes. On account of the small quantity which is obtained—a tree yields from 1·5 to 6·5 kilos., and sometimes does not contain any—and the high price —£3 10*s.* to £7 per kilo., according to the quality—it does not find a market in Europe.

It can however be readily prepared from ordinary camphor. Berthelot obtained Borneo-camphor, together with campholic acid, by treating camphor with alcoholic potash:

$$2C_{10}H_{16}O + KOH = C_{10}H_{18}O + C_{10}H_{15}O_2K.$$

He therefore assumed that camphor is the aldehyde corresponding to borneol or camphyl alcohol.[1]

Baubigny then found, that when sodium is added to a solution of camphor in coal-tar naphtha, sodium borneol and sodium camphor are formed:

$$2C_{10}H_{16}O + 2Na = C_{10}H_{17}ONa + C_{10}H_{15}ONa.$$

Carbon dioxide acts upon this mixture at 100° with formation of the sodium salts of camphorcarboxylic acid, $C_{10}H_{15}O.CO_2H$, and of borneolcarboxylic acid, $C_{10}H_{17}O.CO_2H$, the latter of which is decomposed by water into sodium bicarbonate and borneol.[2]

[1] *Ann. Chem. Pharm.* cxii. 356.
[2] *Compt. Rend.* lxiii. 221; Kachler, *Ann. Chem. Pharm.* cxcvii. 99.

Borneol however is most easily obtained by heating an alcoholic solution of camphor with sodium,[1] the following method being employed:

"Fifty grammes of camphor are dissolved in 500 cb. cms. of alcohol of 96 per cent. in a capacious flask, fitted with a wide reversed condenser, through which 60 grms. of sodium are gradually added in small pieces. The operation must last for about an hour and the rise of temperature not be prevented by cooling; it is, in fact, advisable to accelerate the completion of the reaction by finally adding about 50 grms. of water, the mixture being well agitated during this process."

The product is then poured into 3—4 litres of cold water, the separated borneol collected on a filter cloth, well washed and crystallized from petroleum-ether after drying.[2]

Borneol is a constitutent of the ethereal oil of the Virginian snake-root (*Aristolochia serpentaria*).[3] It is very slightly soluble in water, readily in alcohol and ether and possesses an odour which resembles that of camphor and of pepper, or, according to other authorities, of patchouli. It separates from petroleum-ether in splendidly formed crystals, which usually have a tabular habit. It melts at 206°—207°,[4] and boils at 212°, but volatilizes very rapidly below its melting-point and sublimes in six-sided plates, while it is less volatile than camphor at the ordinary temperature. It is converted into camphor by the action of dilute nitric acid.

Both these substances are optically active and dextrorotatory, while Ngai camphor consists of lævorotatory borneol.[5] This substance, which comes into the market in the form of white grains, is obtained in Canton and the Island Hainan from *Blumea balsamifera*, one of the tall herbaceous Compositæ, and is employed in medicine and as an ingredient of Indian ink. A less pure variety, which is called Bang Phien, forms crystalline masses, saturated with a greenish oil, and has a still more powerful odour than Ngai camphor.

Lævoborneol also occurs in the ethereal oil of *Matricaria parthenium*,[6] in oil of lavender, oil of spike, oil of rosemary,

[1] Jackson and Menke, *Ber. Deutsch. Chem. Ges.* xvi. 2930; Jackson, *ibid.* xviii. Ref. 335; Immendorff, *ibid.* xvii. 1036.
[2] Wallach, *Ann. Chem. Pharm.* ccxxx. 225.
[3] Spica, *Gaz. Chim. Ital.* xvii. 313.
[4] Wallach, *Ann. Chem. Pharm.* ccxxxix. 226.
[5] Plowman, *Jahresb. Chem.* 1874, 537.
[6] Dessaignes and Chautard, *Ann. Chem. Pharm.* lxviii. 342; Haller, *Compt. Rend.* ciii. 64; civ. 109.

and madder fusel oil ;[1] it is formed in small quantity, together with dextroborneol, by the action of sodium on camphor.[2]

Its lævorotation is exactly equal in amount to the dextrorotation of ordinary borneol, and it yields lævorotatory camphor on oxidation. When succinic acid is distilled with caustic potash, a faintly dextrorotatory borneol is formed in small quantity.[3] According to Haller, this is a mixture of both the active forms, while an inactive borneol,[4] probably consisting of equal amounts of both modifications, is obtained by the distillation of crude colophene, a product of the action of sulphuric acid on oil of turpentine.

If borneol be dissolved in cold petroleum-ether and treated with bromine, *borneol bromide*, $C_{10}H_{18}Br_2O$, separates out in yellowish-red plates or needles, which soon decompose with formation of bornyl bromide and other products. Borneol also combines with hydrobromic acid to form the compound $(C_{10}H_{18}O)_2HBr$, which is a crystalline powder, as is also the corresponding hydriodic acid derivative. Both of these substances are decomposed by water with separation of borneol. Wallach was unable to prepare any compound with hydrochloric acid.

According to earlier statements, borneol is converted by heating with phosphorus pentoxide into *borneëne*, $C_{10}H_{16}$, a liquid boiling at 176°—180°. Wallach has found that this substance does not exist, since the product, which is also obtained by the action of phosphorus pentoxide on camphene, is a complicated mixture, probably containing cymene. Pure camphene is formed when borneol is heated with acid potassium sulphate.

2514 *Sodium bornylate*, $C_{10}H_{17}ONa$, is formed when borneol is dissolved in light coal-tar oil and heated with sodium. On the evaporation of the solution it separates in six-sided plates, which dry to a loose mass. It is soluble in water but is rapidly decomposed with separation of borneol. When dry carbon dioxide is passed into its solution in coal-tar naphtha heated to 130° and the temperature then allowed to fall to 100°, *sodium borneolcarboxylate*, $C_{10}H_{17}O.CO_2Na$, separates out as a crystalline mass, which is soluble in cold water. If the solution be allowed to stand for some time, borneol crystallizes out in lustrous plates and sodium bicarbonate is formed.[5]

[1] Jeanjean, *Ann. Chem. Pharm.* ci. 95.
[2] Montgolfier, *Ann. Chim. Phys.* [5] xiv. 21.
[3] Berthelot and Buignet, *Ann. Chem. Pharm.* cxiv. 244.
[4] Armstrong and Tilden, *Ber. Deutsch. Chem. Ges.* xii. 1755.
[5] Kachler and Spitzer, *Monatsh. Chem.* ii. 223.

Methyl bornyl ether, $C_{10}H_{17}OCH_3$, was obtained by Baubigny by the action of methyl iodide or sodium bornylate, as a liquid boiling at 194·5°.[1]

Ethyl bornyl ether, $C_{10}H_{17}OC_2H_5$, is formed in a similar manner, and also, together with camphene, when pinyl chloride (from terebentene) is treated with alcohol and sodium acetate (p. 417). It boils at 205°—208°, is dextrorotatory and decomposes on heating with concentrated hydrochloric acid into ethyl chloride and bornyl chloride.

Dibornyl ether or *Bornyl oxide*, $(C_{10}H_{17})_2O$, is, according to Bruylants, a constitutent of oil of valerian (see below), and is a thick liquid, which boils at 285°—290° and is unaltered by fusion with caustic potash.

Bornyl chloride, $C_{10}H_{17}Cl$, is formed by heating borneol with fuming hydrochloric acid to 100°,[2] and by the action of phosphorus pentachloride upon it,[3] low boiling petroleum-ether being in this case used as a diluent to prevent the formation of oily by-products.[4] Bornyl chloride is also formed when hydrochloric acid is passed into a solution of camphene in absolute alcohol or ether.[5] It is a mass, which appears like camphor, melts at 157° and dissolves readily in ether and petroleum-spirit, less readily in alcohol, from which it separates in thread-like crystals. It differs from pinyl chloride in its much greater instability.

Bornyl bromide, $C_{10}H_{17}Br$, was prepared by Kachler by heating borneol with fuming hydrobromic acid to 100°; it resembles the chloride, but melts at 74°—75°.

Bornylsulphuric acid, $C_{10}H_{17}SO_4H$. Among the products formed by the action of sulphuric acid on French oil of turpentine is *pinyl sulphate*, $(C_{10}H_{17})_2SO_4$, which is converted by heating with alcoholic potash into potassium bornylsulphate, $C_{10}H_{17}SO_4K$. This salt crystallizes in fine plates and is not readily soluble in cold water.[6]

Bornyl carbonate, $(C_{10}H_{17})_2CO_3$, is formed, together with the carbamate, by the action of cyanogen on sodium bornylate and treatment of the product with water. It crystallizes in six-sided tablets or plates, which melt at 215° and are dextrorota-

[1] *Bull. Soc. Chim.* [2] x. 110 and 210.
[2] Berthelot, *Ann. Chem. Pharm.* cxii. 366.
[3] Kachler, *ibid.* cxcvii. 92.
[4] Wallach, *ibid.* ccxxx. 231.
[5] Riban, *Ann. Chim. Phys.* [5] vi. 363; Kachler and Spitzer, *Ann. Chem. Pharm.* cc. 345.
[6] Bouchardat and Lafont, *Compt. Rend.* cv. 1177.

tory. Ngai camphor is even more easily converted into a lævorotatory carbonate, which also melts at 215°.

Bornyl carbamate, $C_{10}H_{17}O.CO.NH_2$, crystallizes in monosymmetric prisms, which show positive hemihedral faces and melt at 115°, while the substance derived from lævoborneol is negatively hemihedral and melts at 126°—127°.[1]

Bornyl acetate, $C_{10}H_{17}.O.C_2H_3O$, is formed when borneol is heated to 150° with acetic anhydride,[2] and by the action of silver acetate on the chloride[3] or of acetyl chloride on borneol.[4] It is a thick, pleasant-smelling liquid, which boils at 227° and crystallizes on standing for some time in masses, which melt at 24.°

According to Bruylants, this ether also occurs in oil of valerian (*Valeriana officinalis*) and boils at 235°—240°. Gerhardt succeeded in proving the presence in it of a terpene, valerianic acid and borneol, the last being only found in old samples or after treatment with caustic potash.[5] Bruylants has now detected, in addition to these, dibornyl ether, the acetate and the two following substances:[6]

	Melting-point.
Bornyl formate, $C_{10}H_{17}.O.CHO$	225°—230°
Bornyl valerate, $C_{10}H_{17}.O.C_5H_9O$ . . .	255°—260°

Haller states that the borneol separated from these ethers is identical with Ngai camphor.[7]

By the continued heating of the so-called terebene (p. 410) with glacial acetic acid, Bouchardat and Lafont obtained a bornyl acetate, which smells like thyme, boils at 215° and yields an inactive borneol on saponification.[8]

2515 *α-Bornylamine*, $C_{10}H_{17}.NH_2$, is formed when camphor, which is the ketone corresponding to borneol, is heated for some hours to 220°—240° with twice its weight of ammonium formate, *α*-bornylformamide being the first product:

$$C_{10}H_{16}O + 2NH_4.CHO_2 = C_{10}H_{17}.NH.CHO + (NH_4)HCO_3 + H_2O$$

This substance is converted by boiling with hydrochloric acid into *α*-bornylamine hydrochloride, from which the base may be set free by caustic potash. It is also obtained by the action of

[1] Haller, *Compt. Rend.* xcii. 1511; xciv. 869; xcviii. 578.
[2] Montgolfier, *Ann. Chim. Phys.* [5] xiv. 5.
[3] Kachler and Spitzer, *loc. cit.*
[4] Schrötter, *Monatsh. Chem.* ii. 224.
[5] *Ann. Chem. Pharm.* xlv. 34.
[6] *Ber. Deutsch. Chem. Ges.* xi. 452.
[7] *Compt. Rend.* ciii. 151.
[8] *Ibid.* cii. 171.

sodium on an alcoholic solution of camphoroxime. On evaporation of its ethereal solution, the *a*-bornylamine is left as a brittle mass resembling camphor and possessing an odour which resembles those of camphor and piperidine. It melts at 158°—160° and boils at 199°—200°, but volatilizes tolerably quickly even at the ordinary temperature.

It is lævorotatory, almost insoluble in water, to which it imparts an alkaline reaction, and rapidly absorbs carbon dioxide from the air.

a-Bornylamine hydrochloride, $C_{10}H_{17}.NH_3Cl$, forms small needles, which are readily soluble in water and alcohol, but insoluble in ether. It combines with platinum chloride and mercuric chloride to form double salts, which, like the other salts of bornylamine, crystallize well.

a-Bornylformamide, $C_{10}H_{17}.NH(CHO)$, is also obtained by heating the base with formic acid; it crystallizes from water in lustrous plates, melting at 61°.

a-Bornylacetamide, $C_{10}H_{17}.NH(C_2H_3O)$, separates from dilute alcohol in small plates, melting at 141°.

a-Bornylcarbamide, $C_{10}H_{17}.NH.CO.NH_2$, is formed when the chloride is boiled with a solution of potassium cyanate; it crystallizes on cooling in needles, which melt at 164.°

Other near derivatives of bornylamine have also been prepared. Bornylamine is a primary amine and gives a very well marked carbamine reaction with chloroform and alcoholic potash.[1]

β-Bornylamine or *camphylamine*, $C_{10}H_{17}.NH_2$, is obtained by the action of sodium on an alcoholic solution of camphoroxime anhydride, $C_{10}H_{15}N$ (p. 430), and is an ammoniacal smelling liquid, which boils at 194°—196° and is readily converted into a solid mass by absorption of carbon dioxide.

β-Bornylamine hydrochloride, $C_{10}H_{17}.NH_3Cl$, is readily soluble in water and crystallizes in thin rhombic plates. The other salts and double salts also crystallize well.

β-Bornylbenzamide, $C_{10}H_{17}.NH(CO.C_6H_5)$, crystallizes in prisms, melting at 75°—77°.[2]

Similarly to the *a*-compound, camphylamine behaves in every respect as a primary amine. The isomerism of the two substances will be subsequently explained.

2516 *Camphor*, $C_{10}H_{16}O$. This compound, which is sometimes termed Chinese camphor and Japanese camphor, or Laurel

[1] Leuckart and Bach, *Ber. Deutsch. Chem. Ges.* xx. 104.
[2] Goldschmidt and Schulhof, *ibid.* xviii. 3297; xix. 708.

camphor, was unknown to the Greeks and Romans. It is first mentioned in the sixth century by Arabian writers and by Aëtios of Amida in Mesopotamia, according to whom Caphura[1] is a rare and valuable medicine. It is again mentioned, together with musk, amber and sandal wood, among the treasures taken in the year 636 by the Kalif Omar at the plundering of the Sassanides palace in Madain on the Tigris, and is subsequently noticed as a costly gift often presented by Indian princes to high Chinese officials. This camphor came from the land known as Kaïsur, the present Sumatra, and was doubtless Borneo-camphor. The fact that camphor is also obtained from China is first mentioned by Avicenna; it was brought into Europe by the Arabians, and St. Hildegard in the twelfth century terms it Ganphora. Marco Polo was acquainted with both kinds of camphor; he states that the camphor from Kaïsur is the most valuable, being sold for its weight in gold, adding that the Chinese variety is obtained in the south-eastern districts of the country from the camphor tree. Garcia de Orta, in 1653, reports that only the Chinese camphor is sent to Europe, that from Borneo and Sumatra being a hundred times more valuable, and Kämpfer, who lived in Japan between the years 1690 and 1692, drew special attention to the difference between the two varieties. In spite of these statements, its vegetable origin was long discredited. Agricola classes it with earth-resin and petroleum, "for from such materials camphor is probably obtained by sublimation; the supposition entertained by some that it is a vegetable resin or gum, is contradicted by the fact that heat is employed in its preparation, for noble constituents are not extracted in this way from the vegetable but rather from the mineral kingdom."

The camphor tree (*Laurus camphora* L., *Cinnamonum camphora*, Nees et Ebermaier) is distributed throughout the eastern provinces of Central China, on the island of Hainan and very extensively in Formosa. It also occurs as a forest tree on the islands Kiushiu and Shikoku of South Japan, its growth being much more vigorous there than in the more northern districts.

The camphor is frequently found collected in rifts in the stem of the tree and is accompanied by an ethereal oil, rich in dipentene (Wallach), which holds it in solution. It also contains lævopinene and *camphorogenol*, $C_{10}H_{18}O_2$, a tolerably heavy oil, which smells somewhat like camphor, but more agreeably, boils

[1] The word camphor or camphora is derived from the Arabic Káfúr, and this probably from the Sanscrit Kapūra—white.

at 212°—213°, and is partially polymerized on continued heating and partially converted into camphor, which is also formed by its oxidation.[1]

The camphor which is prepared on the continent of China is not exported to Europe. This market is however supplied from Formosa, where a very rude method of extraction is in vogue. The trees are felled, cut up into small pieces and these spread on a perforated board, which is cemented with clay over a wooden trough, prepared from the stem of the camphor tree and caulked with clay. Water is heated to boiling in this trough and the steam passing through the branches and pieces of wood carries off the camphor, which is condensed in a tolerably pure state, but with great loss, in pots inverted on the board. No less than 816,587 kilos. of crude camphor were exported from Formosa in the year 1878.

Japan produces about the same quantity. It used to be extracted, according to Kämpfer, by boiling the wood with water in an iron kettle and condensing the vapour in an earthenware dome, closed at the top with rice straw. An earthenware retort is now employed in which the wood is boiled with water; it is fitted with a wooden dome from which the vapours are led through a bamboo tube to the cooling apparatus. This consists of a wooden box containing seven transverse compartments, and is enclosed by a second box through which water is allowed to flow. The vapours are conducted through all the compartments in succession by means of holes placed alternately at either end of the dividing walls.

The crude camphor is usually refined in Europe by mixing it with lime, charcoal, or iron filings and subliming the mixture in large glass vessels,[2] cakes weighing 4—6 kilos. being thus obtained.

A more recent process now adopted in England and America is to sublime it from iron retorts into a cooled chamber, in the same way as flowers of sulphur, the crystalline sublimate being afterwards pressed by hydraulic power into solid disks.[3]

Camphor also occurs, together with borneol, in oil of spike (*Lavandula spica*), oil of lavender (*Lavandula vera*),[4] oil of

[1] Yoshida, *Journ. Chem. Soc.* 1885, i. 779. Borneo camphor is also accompanied by an oil, which appears to be a mixture of two terpenes. It resembles oil of camphor, but does not smell of sassafras as this does. (Flückiger and Hanbury, *Pharmacographia*, 517.)

[2] These are called "Bombolas," an expression which points to a Venetian origin.

[3] Flückiger, *Pharmacognosie*, 137.

[4] Dumas, *Ann. Chem. Pharm.* vi. 248; Lallemand, *ibid.* xiv. 197; Bruylants, *Journ. Chem. Soc.* xxxvi. 725; xxxviii. 50.

rosemary (p. 417), and oil of sage (*Salvia officinalis*).[1] It is obtained artificially by the oxidation of borneol[2] or cymene[3] with nitric acid, and by the treatment of camphene with platinum black[4] or chromic acid solution.[5]

2517 Camphor forms a tough crystalline mass of characteristic taste and odour, and can only be powdered when it is moistened with alcohol or some other solvent. It dissolves in 1,300 parts of water at 20°, and at 12° in 0·8 parts of alcohol of sp. gr. 0·806. It is readily soluble in ether, acetone, chloroform, benzene and other hydrocarbons, as also in glacial acetic acid and in carbon disulphide. It melts at 175°, and boils at 204°, but volatilizes very rapidly at the ordinary temperature and sublimes when kept in closed vessels in lustrous, hexagonal crystals which frequently form splendid stars. This volatility probably also explains the fact that a small piece thrown upon water rotates rapidly until it has completely dissolved. This does not occur if the water be covered with a film of fat, &c., so that crude camphor often does not show the phenomenon. On the other hand it rotates when thrown on mercury and when it is placed on a small piece of wood floating on water.[6]

The solutions of camphor are dextrorotatory; the corresponding lævorotatory modification is formed by the oxidation of lævocamphene, while the inactive camphene yields an inactive camphor.[7] Lævoborneol, on the other hand, is converted into ordinary camphor by oxidation.[8]

When camphor is heated with phosphorus pentoxide, it is resolved into cymene and water (p. 27), a decomposition which is also brought about by heating with concentrated hydrochloric acid to 170°.[9] If zinc chloride be employed, however, benzene, toluene, xylene, pseudocumene, and laurene, $C_{11}H_{16}$ (p. 346), are formed in addition.[10] The same products, with the exception of laurene, are formed when camphor is heated with zinc dust.[11] Iodine acts upon it, when the mixture is heated, with evolution of hydriodic acid and formation of cymene, carvacrol (p. 295),

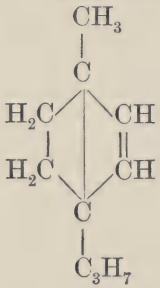
[1] Muir, *Journ. Chem. Soc.* xxxvii. 685.
[2] Pelouze, *Ann. Chem. Pharm.* xl. 328.
[3] Oppenheim, *Ber. Deutsch. Chem. Ges.* v. 631.
[4] Berthelot, *Ann. Chem. Pharm.* cx. 367.
[5] Riban, *Bull. Soc. Chim.* xxiv. 19.
[6] Tomlinson, *Chem. News*, lii. 50.
[7] Armstrong and Tilden, *Ber. Deutsch. Chem. Ges.* xiii. 1756.
[8] Montgolfier, *Ann. Chim. Phys.* [5] xiv. 29.
[9] Alexejew, *Beilstein's Handb.* 1763.
[10] Fittig, Köbrich and Jilke, *Ann. Chem. Pharm.* cxlv. 29.
[11] Schrötter, *Ber. Deutsch. Chem. Ges.* xiii. 1621.

laurene and other bodies, the exact nature of which has not yet been ascertained.[1] If a somewhat higher temperature, about 250°, be employed in this reaction, inflammable gases are evolved in considerable amount and the hydrocarbons mentioned above, accompanied by others, are formed.[2] The action of other reagents upon camphor will be subsequently mentioned. It is frequently employed in Eastern Asia as incense, while it finds application with us as a medicine, used both externally and internally. Like other analogous compounds it has a strong antiseptic action and also serves to prevent the ravages of clothes-moths and other insects, and for this reason it is largely used in natural history museums.

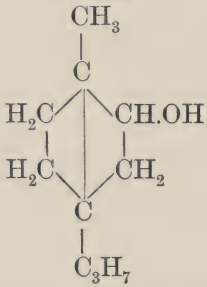
Administered to a dog, it appears in the urine as *camphoglucuronic acid*, $C_{16}H_{24}O_8$, and *uramidocamphoglucuronic acid*, the composition of which has not yet been determined. The former of these on boiling with dilute hydrochloric acid yields *camphorol*, $C_{10}H_{16}O_2$, which crystallizes in thin tablets, melts at 197°—198°, readily sublimes and is converted by oxidation into camphoric acid.[3]

The constitutions of camphene, borneol and camphor may be expressed by the following formulæ :[4]

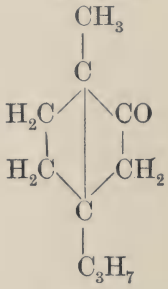
Camphene.



Borneol.



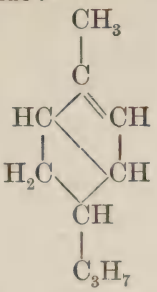
Camphor.

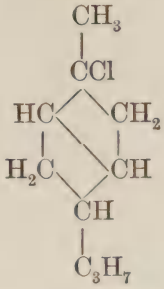


Camphene combines with hydrochloric acid to form bornyl chloride and borneol is converted by oxidation into camphor, which is the ketone corresponding to this alcohol. Further proofs of the accuracy of those formulæ will be subsequently adduced. Pinene, in a similar manner, combines with hydrochloric acid to form pinyl chloride and this is converted by elimination of hydrochloric acid into camphene. The following constitu-

[1] Armstrong and Gaskell, *Ber. Deutsch. Chem. Ges.* xi. 151.
[2] Preis and Raymann, *ibid.* xiii. 346.
[3] Schmiedeberg and Meyer, *Hoppe-Seyler's Zeitschr.* iii. 422.
[4] Wallach, *Ann. Chem. Pharm.* ccxxx. 269.

tion must therefore probably be assigned to pinene and its hydrochloride :[1]





Camphene is thus formed from pinyl chloride by elimination of hydrochloric acid and rearrangement of the double linking. The fact that pinene and camphene only contain one ethylene linking is also confirmed by their specific refractions.[2]

2518 *Camphidene dichloride*, $C_{10}H_{16}Cl_2$. This compound, which is usually called *camphor dichloride*, is formed, according to Gerhardt, by the action of phosphorus pentachloride on camphor. Pfaundler then found that the compound, $C_{10}H_{15}Cl$,[3] is thus formed if the mixture be heated and that cymene passes over when the distillation is slowly conducted.[4] Spitzer, on the other hand, observed that several higher chlorinated compounds are formed when the mixture is heated, but the dichloride can readily be obtained pure by avoiding any rise of temperature ;[5] it is also formed by the treatment of bornyl chloride with chlorine,[6] a reaction which corresponds to the formation of ethidene chloride from ethyl chloride.

Camphidene dichloride crystallizes from alcohol in fine needles, while it separates from ether in large rhombic crystals. It melts at 155°, readily loses hydrochloric acid in the moist state, and is converted by the action of alkyl iodides and sodium into homologues of camphene. In the formation of these substances, hydrochloric acid and chlorocamphene are first produced and substitution then takes place. The following have been prepared by Spitzer :

	Boiling-point.
Ethylcamphene, $C_{10}H_{15}.C_2H_5$	198°—200°
Isobutylcamphene, $C_{10}H_{15}.C_4H_9$ . . .	228°—229°

[1] Wallach, *Ann. Chem. Pharm.* ccxxxix. 49.
[2] Brühl, *Ber. Deutsch. Chem. Ges.* xxi. 145.
[3] *Ann. Chem. Pharm.* cxv. 29.
[4] Luginin and Lippmann, *ibid. Suppl.* v. 260.
[5] *Ibid.* cxcvi. 262 ; *Monatsh. Chem.* i. 319.
[6] Kachler and Spitzer, *Ann. Chem. Pharm.* cc. 240.

Camphidenoxime or *Camphoroxime*, $C_{10}H_{16}N.OH$, is formed when a concentrated aqueous solution of hydroxylamine hydrochloride is mixed with an alcoholic solution of camphor, sodium carbonate added until the reaction is alkaline and the solution diluted with alcohol and allowed to stand eight days. It is then precipitated with water or evaporated and the residue extracted with ether. On the evaporation of the latter, camphoroxime crystallizes out in white needles, while it separates from alcohol in transparent, sword-shaped prisms, which smell like camphor and also rotate on water. It melts at 115° and boils with slight decomposition at 249°—254°.[1]

Camphoroxime hydrochloride, $C_{10}H_{16}N(OH)HCl$, forms a white voluminous powder, which is only slightly soluble in water, readily in alcohol and acids.

Sodium camphoroximate, $C_{10}H_{16}N(ONa)$, is obtained by the addition of an alcoholic sodium solution to an ethereal solution of the oxime. It forms a white powder, which is only slightly soluble in cold, but readily in hot alcohol and water.

Ethyl camphoroximate, $C_{10}H_{16}N(OC_2H_5)$, is formed by heating the sodium salt with alcohol and ethyl iodide; it is a pleasantly smelling liquid, boiling at 208°—210°.

Camphoroxime anhydride, $C_{10}H_{15}N$, is formed by the action of acetyl chloride on camphoroxime[2] and by allowing it to remain in contact with acids for some time.[3] It is a faintly smelling liquid, boiling at 216°—218°, which combines with hydroxylamine to form a substance of the formula $C_{10}H_{18}N_2O$. This compound crystallizes in white plates, melts at 101° and dissolves in alkalis and acids.

Isocamphoroxime, $C_{10}H_{17}NO$, is prepared by heating the anhydride with alcoholic potash; it forms inodorous plates, which are slightly soluble in hot water, readily in alcohol, ether and strong acids,[4] melt at 125° and are not attacked by heating with methyl iodide and sodium ethylate.[5] It is reconverted into the anhydride by distillation with phosphorus pentasulphide.

2519 *Hydroxycamphor*, $C_{10}H_{16}O_2$, was obtained by Kachler and Spitzer by the action of sodium amalgam on an alcoholic solution of β-dibromocamphor,[6] $C_{10}H_{14}Br_2O$. Goldschmidt and Zürrer then found that an isomeric compound is formed by boiling camphoroxime anhydride with alcoholic potash. This

[1] Nägeli, *Ber. Deutsch. Chem. Ges.* xvi. 497.
[2] Nägeli, *ibid.* xvi. 2981.
[3] Leuckart and Bach, *ibid.* xx. 110.
[4] Goldschmidt and Zürrer, *ibid.* xvii. 2069.
[5] Nägeli, *ibid.* xvii. 805.
[6] *Monatsh. Chem.* iii. 205.

they termed *campholenic acid*, but it was proved by Kachler and Spitzer to be identical with hydroxycamphor. It forms a faint yellow liquid, which boils at 265°, smells like turpentine and possesses weak acid properties. When its ammonium salt is heated to 250°, isocamphoroxime is formed. To explain this fact, Goldschmidt and Zürrer look upon the iso-oxime as the amide of campholenic acid, camphoroxime anhydride being the corresponding nitril:

Campholenic acid.	Campholenamide.	Campholene nitril.
$C_9H_{15}.CO_2H$	$C_9H_{15}.CO.NH_2$	$C_9H_{15}.CN$

This appears, however, to be improbable, since, according to this view, camphor would simply be campholenaldehyde, $C_9H_{15}.CHO$, whereas it is undoubtedly a ketone. The formation of all the compounds described above may be explained by the following series of equations:

Camphor. Camphoroxime.

$$C_8H_{14}\begin{cases}CO\\|\\CH_2\end{cases} + H_2N.OH = C_8H_{14}\begin{cases}C{=}N.OH\\|\\CH_2\end{cases} + H_2O.$$

Camphoroxime. Camphoroxime anhydride.

$$C_8H_{14}\begin{cases}C{=}N.OH\\|\\CH_2\end{cases} = C_8H_{14}\begin{cases}-C-\\|\\CH\end{cases}\!\!>N + H_2O.$$

Isocamphoroxime.

$$C_8H_{14}\begin{cases}-C-\\|\\CH\end{cases}\!\!>N + H_2O = C_8H_{14}\begin{cases}CO\\|\\CH.NH_2\end{cases}.$$

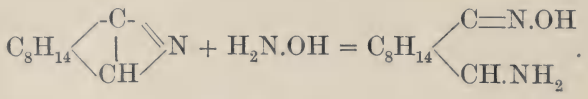
Hydroxycamphor.

$$C_8H_{14}\begin{cases}CO\\|\\CH.NH_2\end{cases} + H_2O = C_8H_{14}\begin{cases}CO\\|\\CH.OH\end{cases} + NH_3$$

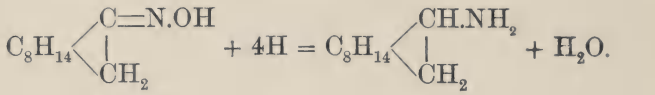
$$5C_8H_{14}\begin{cases}CO\\|\\CH.NH_2\end{cases} + P_2S_5 = 5C_8H_{14}\begin{cases}-C-\\|\\CH\end{cases}\!\!>N + P_2O_5 + 5H_2S.$$

Goldschmidt and Zürrer, to support their view that the anhydride is a nitril, adduce the fact that it combines with hydroxylamine to form the amidoxime, $C_9H_{15}.C\begin{cases}N.OH\\NH_2\end{cases}$.

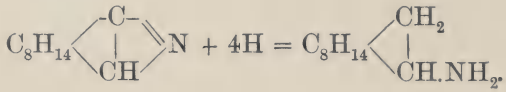
The formation of this compound, however, may be simply explained in the following manner:



The isomerism of bornylamine and camphylamine may also be explained upon these lines.[1] The former is obtained by replacing the oxygen of camphor by the amido-group and by the reduction of the oxime:

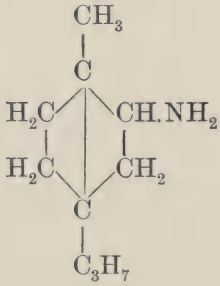


Camphylamine, on the other hand, is obtained by the action of hydrogen on the anhydride:

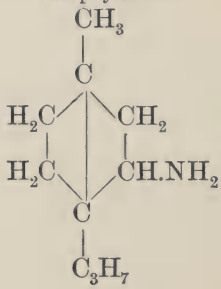


The difference between these substances depends therefore on an isomerism of position, which is more clearly shown by the following formulæ:

Bornylamine.



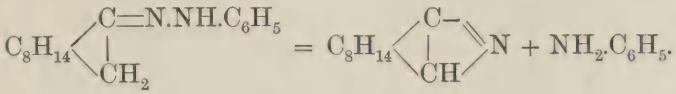
Camphylamine.



Camphorhydrazone, $C_{10}H_{16}{=}N_2H.C_6H_5$, is formed when an alcoholic solution of camphor is treated with a solution of phenylhydrazine and sodium acetate and then heated. It is an oily liquid, which boils at 235°—243° at a pressure of 17 mm.

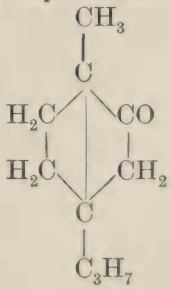
[1] Leuckart and Bach, *Ber. Deutsch. Chem. Ges.* xx. 104.

and is decomposed by dry hydrochloric gas into aniline and camphoroxime anhydride :[1]

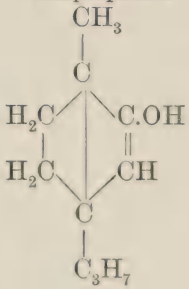


Whilst in the formation of the substances hitherto described camphor acts as a ketone or camphidene oxide, it behaves in many cases as *camphophenol :*

Camphidene oxide.



Camphophenol.



The latter does not exist in the free state, and we have therefore a similar case to those of phloroglucinol and isatin, with the difference that in these the ketone form is the unstable one, while again in the case of carvol and carvacrol both forms exist.

Sodium camphophenate, $C_{10}H_{15}ONa$, usually called sodium camphor, is formed, as already described, together with sodium bornylate by the addition of sodium to a solution of camphor in benzene or toluene. If the product be treated with ethyl iodide, a mixture of bornyl ethyl ether and *ethylcamphor* or *ethyl camphophenate,* $C_{10}H_{15}.OC_2H_5$, is formed. The latter is a liquid, which has a similar smell to camphor and boils at 226°—229°.

2520 *Chlorocamphor,* $C_{10}H_{15}ClO$, was obtained by Wheeler by the action of hypochlorous acid on camphor. It separates from alcohol as a crystalline powder, melts at 95° and decomposes at 200°. It is converted by the action of alcoholic potash into a hydroxycamphor, $C_{10}H_{16}O_2$, which crystallizes in small needles, melting at 137°, smells like camphor and is volatile with steam.[2]

Cazeneuve then found that when chlorine is passed into a

[1] Balbiano, *Ber. Deutsch. Chem. Ges.* xviii. Ref. 663 ; xix. Ref. 553.
[2] *Ann. Chem. Pharm.* cxlvi. 73.

solution of camphor in absolute alcohol, two monochlorocamphors are formed, one of which crystallizes from alcohol in long, white needles or large monosymmetric prisms, which melt at 83°—84°. It smells like camphor, has an aromatic, bitter taste, boils at 244°—247° and is volatile with steam. The other modification, which is formed in smaller quantity, forms microscopic crystals, melts at 100° and boils at 230°—237°. It is converted by treatment with alcoholic potash into the first modification, and Cazeneuve therefore assumes that the isomerism is of a physical nature. Nascent hydrogen reconverts chlorocamphor into camphor.[1]

Schiff and Puliti then treated an alkaline solution of camphocarboxylic acid (see below) with chlorine and obtained a chlorocamphor, which also crystallizes in large prisms, but does not melt until 93°—94°, its behaviour in other respects being however identical with that of Cazeneuve's compound.[2]

These two compounds are considered by Balbiano to be identical, since they are both converted by phenylhydrazine into camphineosazone, which is described below.[3] They are also both converted into camphoric acid, $C_8H_{14}(CO_2H)_2$, by oxidation.

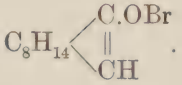
Dichlorocamphor, $C_{10}H_{14}Cl_2O$, also exists in two isomeric forms, which are formed by the action of chlorine on an alcoholic solution of camphor and are physical isomerides (Cazeneuve). One of these crystallizes from alcohol in large, rhombic prisms, which melt at 93°, readily sublime and are only slightly soluble in cold alcohol, while the other is extremely soluble in alcohol and is therefore difficult to obtain in crystals. It melts at 77° and has a dextrorotation equal to that of the higher melting modification.[4]

Trichlorocamphor, $C_{10}H_{13}Cl_3O$, is formed by the action of chlorine on fused chlorocamphor. It forms small, white crystals, melting at 54°.[5]

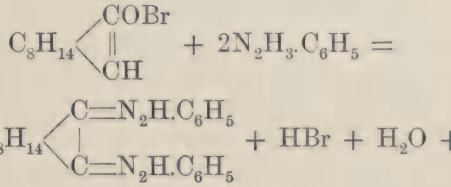
Bromocamphor, $C_{10}H_{15}BrO$. Laurent found that camphor combines with bromine to form the dibromide,[6] which is, however, more readily obtained by employing a solution of camphor in chloroform.[7] It crystallizes in orange-red prisms, which lose bromine in the air and on heating to 100° in a closed vessel decompose into hydrobromic acid and bromocamphor (Swarts). In order to prepare the latter, 30 parts of camphor and 32 parts

[1] *Compt. Rend.* xciv. 1530; xcv. 1358; ci. 438; *Bull. Soc. Chim.* xxxix. 501.
[2] *Ber. Deutsch. Chem. Ges.* xvi. 887.
[3] *Ibid.* xx. Ref. 215.
[4] *Compt. Rend.* xciv. 730, 1360.
[5] Cazeneuve, *ibid.* ciii. 551, 606.
[6] *Ann. Chem. Pharm.* xlviii. 251.
[7] Swarts, *Jahresb. Chem.* 1862, 462.

of bromine are dissolved in 18 parts of chloroform, the latter distilled off after some hours and the residue washed with alcohol and recrystallized from ether.[1] It crystallizes in monosymmetric prisms, isomeric with those of chlorocamphor,[2] which melt at 76° and smell like camphor. It is readily soluble in alcohol and ether, still more freely in chloroform and benzene. It boils at 274°,[3] yields camphoric acid on oxidation and is reconverted into camphor by the action of nascent hydrogen or by heating with alcoholic potash, while sodium converts it into sodium camphophenate. It is not attacked by phosphorus pentachloride even at 100°. It follows from these reactions that bromocamphor has a constitution which resembles that of tribromophenol bromide (Pt. III. p. 116):



It is employed in medicine as a soporific in cases of hysteria, dipsomania, delirium tremens, &c. The isomeric chlorocamphors have the same action[4] and therefore an analogous constitution, this being also confirmed by the fact that they, as well as bromocamphor, are converted into *camphineosazone* by heating with phenylhydrazine:[5]



It forms an amorphous mass, melting at 55°.

Dibromocamphor, $C_{10}H_{14}Br_2O$. Swarts found that this compound, which melts at 114·5°, is formed when monobromocamphor is heated to 120° with bromine. According to other statements, it melts at 57°, and this is confirmed by Schiff, who assumes that the higher number was originally a printer's error

[1] Keller, *Jahresb.* 1880, 726; see also Maisch, *ibid.* 1873, 499; Gault, *ibid.* 1874, 538.

[2] Montgolfier, *Ann. Chim. Phys.* [5] xiv. 110; Cazeneuve and Morel, *Compt. Rend.* ci. 438.

[3] Perkin, *Ann. Chem. Pharm. Suppl.* iv. 125.

[4] *Ber. Deutsch. Chem. Ges.* xx. Ref. 291.

[5] Balbiano, *ibid.* xix. Ref. 553; xx. Ref. 215.

and has been copied from one text-book to another for about fifteen years.[1]

Kachler and Spitzer have however found that dibromocamphor exists in two modifications.[2]

α-Dibromocamphor is formed when monobromocamphor is heated for six to eight hours with the calculated quantity of bromine at 120°. It separates from the brown syrupy product on standing in the form of crystals, which are purified by recrystallization from alcohol. It may be obtained from petroleum spirit in rhombic crystals, which melt at 61°, volatilize with steam and are converted into monobromocamphor and camphor by heating with alcoholic potash or by reduction. It is not attacked by phosphorus pentachloride and is converted into camphocarboxylic acid by the action of sodium and carbon dioxide.

β-Dibromocamphor is obtained by heating the *α*-derivative or monobromocamphor with bromine for 10—12 hours to 125°—130°. It crystallizes in rhombic tablets, melting at 115°, is only slightly volatile with steam and is also not attacked by phosphorus pentachloride. On heating with alcoholic potash, it yields an oily mixture, while it is converted into camphor by the action of sodium on its ethereal solution.

Iodocamphor, $C_{10}H_{15}IO$, is formed by the action of cyanogen iodide on sodium camphor, and forms crystals, which are isomorphous with those of chlorocamphor and melt at 43°—44°.[3]

2521 *Nitrocamphor*, $C_{10}H_{15}(NO_2)O$, is obtained from the following compounds by treating them with alcoholic potash or acting upon them in ethereal solution with zinc and sulphuric acid.[4] It is, however, most advantageous to boil the alcoholic solution with zinc upon which a thin layer of copper has been precipitated. Nitrocamphor crystallizes from alcohol in rhombic prisms, has a strong lævorotation and melts at 100°—101°.[5] According to Schiff, it has the following constitution :

$$C_8H_{14}\begin{cases} C.OH \\ \| \\ C.NO_2 \end{cases}.$$

It is a powerful, monobasic acid, and yields very characteristic salts, which have been investigated by Cazeneuve. They are

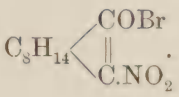
[1] *Ber. Deutsch. Chem. Ges.* xiv. 1378.
[2] *Monatsh. Chem.* iii. 205.
[3] Haller, *Compt. Rend.* lxxxvii. 695.
[4] Schiff, *Ber. Deutsch. Chem. Ges.* xiii. 1402 ; Schiff and Piluti, *ibid.* xvi. 889.
[5] Cazeneuve, *Bull. Soc. Chim.* xlvii. 920 ; xlix. 92.

dextrorotatory and decompose on heating with production of a smell of myrrh. Those of the alkali metals and of magnesium are soluble in water.

The zinc salt, $[C_{10}H_{14}(NO_2)O]_2Zn + H_2O$, crystallizes from alcohol in large, six-sided, apparently rhombic tablets. The copper salt, $[C_{10}H_{14}(NO_2)O]_2Cu + H_2O$, is a chestnut brown precipitate, which forms a solution of this colour in alcohol, from which it separates in small, grass-green crystals. The ferrous salt forms garnet-red tablets, which are probably isomorphous with the zinc salt, while the ferric salt is a blood-red precipitate, which imparts the same colour to alcohol.

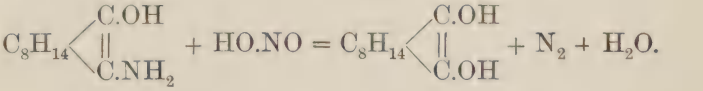
Nitrochlorocamphor, $C_{10}H_{14}Cl(NO_2)O$, is formed by the action of concentrated nitric acid on chlorocamphor, and crystallizes from alcohol in long needles, melting at 93°—94°. An isomeric compound is formed at the same time as a mass, which resembles camphor, melts at 83° and has a bitter aromatic taste.

Nitrobromocamphor, $C_{10}H_{14}Br(NO_2)O$, forms large, rhombic prisms and is isomorphous with the preceding compound and with dichlorocamphor.[1] It melts at 104°—105°, scarcely dissolves in cold alcohol and is insoluble in alkalis, on which account Schiff has assigned the following formula to it:



Amidocamphor, $C_{10}H_{15}(NH_2)O$, is obtained by adding sodium amalgam to a solution of nitrocamphor in strong caustic potash. It is a thick, oily liquid, which boils at 246·4°, solidifies to a waxy mass on cooling, has a penetrating ammoniacal odour and an alkaline reaction and behaves in every respect as a primary amine. Its hydrochloride crystallizes in white needles.

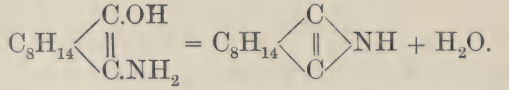
An isomeride of hydroxycamphor, *dihydroxycamphene*, is formed by the action of nitrous acid on the aqueous solution of this base:



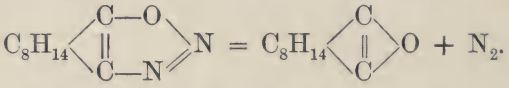
It is a crystalline mass, which melts at 154°—155° and is volatile with steam.

[1] Cazeneuve, *Compt. Rend.* ci. 438.

Camphimide, $C_{10}H_{15}N$, is formed by boiling the hydrochloride of amidocamphor with water:



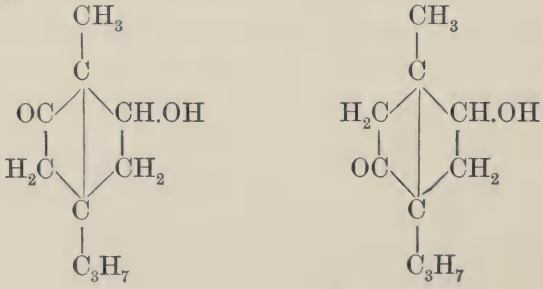
This substance is isomeric with camphoroxime anhydride and forms an oily liquid, which smells like coniine and solidifies at a low temperature. When the solution of its hydrochloride is mixed at 0° with sodium nitrite solution, a compound is precipitated, which crystallizes in large, yellow tablets, melting at 73°—74°, and has the formula $C_{10}H_{14}N_2O$. Schiff considers it to be a diazo-compound and not nitrosocamphimide, since it does not yield a hydrazine by the action of acetic acid and zinc dust, but is reconverted into amidocamphor. When it is heated to 140°, *dehydrocamphor* or *camphine oxide* is formed:



This is a crystalline substance, which melts at 160°, smells like camphor and volatilizes with steam.[1]

Hydroxyisocamphor, $C_{16}H_{15}O(OH)$. The acetate of this compound is formed together with camphor, when bornyl acetate is oxidized in acetic acid solution with chromic acid. It crystallizes in prisms, melting at 69°, boils at 273·5° with slight decomposition and is converted by boiling with caustic potash into hydroxyisocamphor, which remains on the evaporation of the ethereal solution as a crystalline mass. It has a faint odour of vanilla, sublimes readily and melts with decomposition at 248°—249°. It is oxidized by nitric acid to camphanic acid, $C_{10}H_{14}O_4$, (p. 446).[2]

Its constitution is probably expressed by one of the following formulæ:

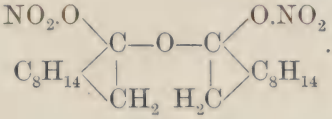


[1] Schiff, *Ber. Deutsch. Chem. Ges.* xiv. 1375.
[2] Schrötter, *Monatsh. Chem.* ii. 224.

Addition-products of camphor. Hydrochloric acid, sulphur dioxide and nitrogen peroxide all combine with camphor to form liquid compounds, which are decomposed by water but have not hitherto been further investigated.

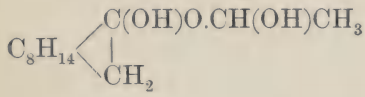
Camphor hydriodide, $C_{10}H_{16}O.IH$, is obtained together with other products (p. 427), by heating camphor with iodine. It forms crystals, which fume in the air and rapidly deliquesce.

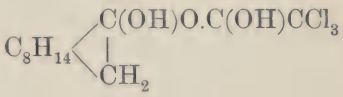
Camphor nitrate, $(C_{10}H_{16}O)_2N_2O_5$. This characteristic compound was first obtained by Brandes, who heated camphor with dilute nitric acid.[1] It is formed, together with camphoric acid, when camphor is boiled with nitric acid of sp. gr. 1·37 in a retort, and distils over as an oily liquid, which has a sour but camphor-like smell, and is decomposed by water with separation of camphor, while dry potassium carbonate has no action upon it. It is volatile with nitric acid without decomposition, but decomposes to a very large extent when distilled alone, nitrous fumes being evolved. Its constitution is without doubt analogous to that of cinnamaldehyde nitrate:



Camphor boronfluoride, $C_{10}H_{16}O.BF_3$, is formed when boronfluoride is passed into fused camphor. It crystallizes in needles, which melt at 70°.[2]

Aldehyde camphor is produced when camphor is shaken up with a solution of aldehyde. It is an oily liquid, which readily loses aldehyde and is decomposed into its constituents by water. When camphor and chloral hydrate are triturated together, a thick liquid is formed, which has a pungent taste, dissolves in alcohol and chloroform and is decomposed by water.[3] These compounds have probably the following constitution:





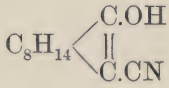
2522 *Cyanocamphor* or *Camphonitril*, $C_{10}H_{15}O(CN)$, is obtained when cyanogen is passed into a hot solution of camphor in

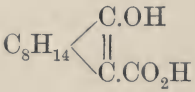
[1] *Schweigg. Journ.* xxxviii. 257. [2] Landolph, *Compt. Rend.* lxxxvi. 539.
[3] Cazeneuve, *Bull. Soc. Chim.* xxxiv. 209; xxxvi. 650.

toluene to which metallic sodium has been added. It crystallizes from ether in rectangular prisms, melts at 127°—128° and boils with decomposition at 250°. If it be dissolved in warm caustic soda solution, *sodium cyanocamphophenate*, $C_{10}H_{14}(ONa)CN$, separates out on cooling in fine needles, which are soluble in alcohol, but are decomposed by water. The potassium salt forms pearly tablets.[1]

Camphocarboxylic acid, $C_{10}H_{15}O(CO_2H)$. This compound was discovered by Baubigny and is obtained by dissolving 150 grams. of camphor in 500 ccms. of toluene, heating the solution to 90°, and finally adding 16 grams. of sodium and passing in carbon dioxide. The product is extracted with water and the solution allowed to stand, until the borneol, which is simultaneously formed, has separated out. It is then filtered, the concentrated solution decomposed with hydrochloric acid and extracted with ether. Impure camphocarboxylic acid remains on evaporation and is recrystallized from hot water, which must not be boiling.[2] It crystallizes from dilute alcohol in long, silky needles and from water and ether in monosymmetric prisms, which melt at 123°—124° and decompose into carbon dioxide and camphor when more strongly heated. It is also formed from dibromocamphor by the action of sodium and carbon dioxide.

Its formation corresponds to that of salicylic acid from phenol, and since its nitril behaves as a phenol, we arrive at the following constitutional formulæ:





Ethyl camphocarboxylate, $C_{10}H_{14}(OH)CO_2.C_2H_5$, was obtained by Haller, who saturated an alcoholic solution of the nitril with hydrochloric acid and allowed the whole to stand; it has also been prepared by Roser from the acid by the same method.[3] It is a liquid, which smells like camphor and boils at 276°.

Chlorocamphocarboxylic acid, $C_{10}H_{14}ClO.CO_2H$, is formed when a current of chlorine is passed into an alkaline solution of the acid. It separates on the addition of dilute hydrochloric acid in white crystalline flocks, which melt at 93°—94° with evolution

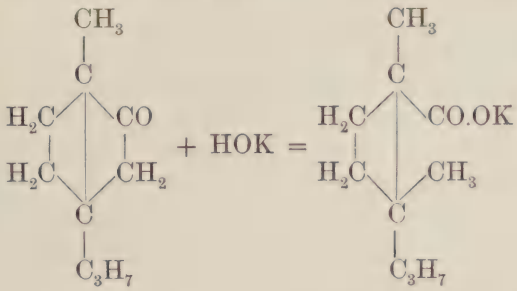
[1] Haller, *Compt. Rend.* lxxxvii. 843; cii. 1477.
[2] Kachler and Spitzer, *Monatsh. Chem.* ii. 233.
[3] *Ber. Deutsch. Chem. Ges.* xviii. 3112.

of gas and decompose completely at 100° into chlorocamphor and carbon dioxide.[1]

Bromocamphorcarboxylic acid, $C_{10}H_{14}BrO.CO_2H$, is obtained when the acid is treated with bromine at a low temperature. It is readily soluble in alcohol and ether and is precipitated by hydrochloric acid from its alkaline solution as a crystalline powder, which decomposes into carbon dioxide and bromocamphor when heated to 65° or boiled with alcohol.

OXIDATION PRODUCTS OF CAMPHOR.

2523 *Campholic acid*, $C_{10}H_{18}O_2$, was obtained by Delalande[2] by passing the vapour of camphor over potash lime heated to 300°—400°. It is also formed by the continued boiling of camphor with alcoholic potash :



It is best prepared, however, by adding sodium to a heated solution of camphor in a rock-oil boiling at 130°. Sodium bornylate and sodium camphor are simultaneously obtained, and constitute the chief product if a lower temperature be employed.[3] The mass which separates out is pressed and treated with water, which precipitates camphor and borneol. These are filtered off and the campholic acid precipitated by the addition of sulphuric acid. It is then finally purified by distillation and recrystallization.[4]

It is scarcely soluble in cold water and crystallizes from dilute alcohol in long brittle prisms, but from a mixture of ether and

[1] Schiff and Puliti, *Ber. Deutsch. Chem. Ges.* xvi. 887 ; J. de Santos e Silva, *ibid.* vi. 1092.
[2] *Ann. Chem. Pharm.* xxxviii. 337.
[3] Malin, *ibid.* cxlv. 201 ; Kachler, *ibid.* clxii. 259.
Montgolfier, *Ann. Chim. Phys.* [5] xiv. 99.

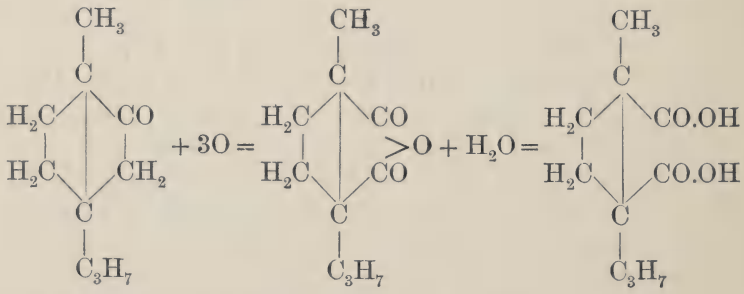
alcohol in soft plates, which melt at 95°, readily sublime and volatilize with steam.

Camphol chloride, $C_{10}H_{17}OCl$, is formed by the action of phosphorus pentachloride on the acid and is an oily liquid, which boils at 222°—226°.

2524 *Camphoric acid*, $C_{10}H_{16}O_4$. Kosegarten, whose *Dissertatio de camphora et partibus quae eam constituunt* appeared in the year 1785, endeavoured so far as possible to dephlogisticate camphor by repeated treatment with nitric acid and thus obtained an acid, which he found to resemble oxalic acid, but nevertheless considered it as a distinct substance. In 1793, Dörfurt concluded that this acid was benzoic acid, but this assertion was contradicted by Bouillon-Lagrange in 1799 and Bucholz in 1809. It was then investigated by many chemists and its composition finally determined by Malaguti, Liebig and Laurent.[1]

Its power of dextrorotation was then observed by Bouchardat.[2] A lævorotatory camphoric acid was then prepared by Chautard by the oxidation of lævocamphor and was found to differ from the previously known modification only in the direction of its rotation of the plane of polarised light. These two substances, like the two tartaric acids, combine to form an inactive para-camphoric acid,[3] and camphoric acid is also converted into an inactive mesocamphoric acid by heating with water in a sealed tube, so that the analogy with tartaric acid is completely borne out.

Camphoric acid is probably formed from camphor according to the following equation:

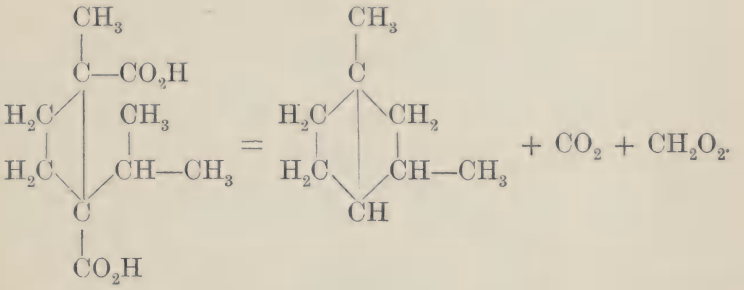


It is also formed by the oxidation of campholic acid with concentrated nitric acid (Kachler).

[1] *Ann. Chem. Pharm.* xxii. 38, 50 and 135.
[2] *Jahresber. Chem.* 1863, 556.
[3] Chautard, *Ann. Chem. Pharm.* cxxvii. 121.

In order to prepare it, camphor is distilled in a retort with ten parts of concentrated nitric acid and the distillate repeatedly replaced in the retort until all the camphor has dissolved and no further evolution of nitrous fumes occurs, fresh portions of nitric acid being added if necessary (Laurent). According to Wreden, 150 grams. of camphor and two litres of nitric acid of sp. gr. 1·27 are brought into flasks of four litres capacity, a conducting tube for the nitrous fumes being fastened in the neck by means of plaster of Paris. The mixture is heated on a briskly boiling water-bath until the vapours are only slightly coloured, the operation lasting for about 50 hours. The product is then converted into the sodium salt and this once recrystallized. About 725—805 grams. of pure camphoric acid are obtained from 1500 grms. of camphor.[1]

It is readily soluble in alcohol; 100 parts of water dissolve 0·625 parts at 12° and 10 parts at the boiling point. It crystallizes in small plates or monosymmetric prisms, melting at 178°. On fusion with caustic potash isopropylsuccinic acid (pimelic acid) is formed. When it is heated with zinc chloride[2] or with distilled hydriodic acid to 200°, tetrahydrometaxylene is obtained, while if the concentrated acid be employed, hexhydrometaxylene is formed.[3] Carbon dioxide and hydrogen are first eliminated, probably to some extent as formic acid, and since camphoric acid contains the isopropyl group, the formation of the so-called tetrahydrometaxylene then admits of a simple explanation:



The conversion of this into hexhydrometaxylene then follows by the addition of hydrogen.

Camphorates. The salts of the alkali metals are very readily

[1] *Ann. Chem. Pharm.* clxiii. 323. [2] Ballo, *ibid.* cxcvii. 321.
[3] Wreden, *ibid.* clxxxvii. 156.

soluble and do not easily crystallize; acid salts of these metals do not appear to exist.

Calcium camphorate, $C_{10}H_{14}O_4Ca + 9H_2O$, forms crystals, which are tolerably soluble in water; when its solution is boiled with camphoric acid, the acid salt, $(C_{10}H_{15}O_4)_2Ca$, is formed and crystallizes in large prisms.

Kemper has also prepared the corresponding barium salts; on the other hand only the normal *magnesium camphorate* has been prepared. It crystallizes with varying amounts of water.[1] The salts of most of the other metals are insoluble or only slightly soluble in water, The soluble salts have less rotatory power than the free acid, while the reverse of this is true in the case of malic acid, tartaric acid, aspartic acid and quinic acid.[2]

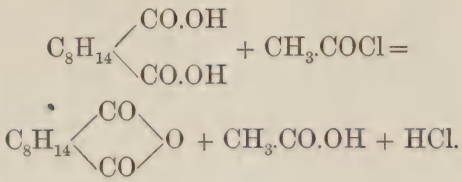
Acid methyl camphorate, $C_{10}H_{15}(CH_3)O_4$, is formed by the distillation of camphoric acid with wood spirit and sulphuric acid. It is thus obtained as a viscid oil, which solidifies after some time in contact with water to a crystalline mass and crystallizes from alcohol in rhombic prisms, melting at 68°. Its alcoholic solution gives crystalline precipitates with lead acetate and copper acetate.[3]

Normal ethyl camphorate, $C_{10}H_{14}(C_2H_5)_2O_4$. The acid ether is obtained by the distillation of camphoric acid with alcohol and sulphuric acid as a thick, colourless liquid, which decomposes on distillation into camphoric anhydride and the normal compound. This is an oily liquid, which boils at 285°—287° and has an unpleasant, almost unbearable smell and a very disagreeable, bitter taste.[4]

2525 *Camphoryl oxide*, $C_{10}H_{14}O_3$. The anhydride of camphoric acid was obtained as early as the year 1799 by Bouillon-Lagrange from the acid by simple distillation, and it was then further investigated by Malaguti and by Laurent. Gerhardt and Chiozza, who also examined it, found that it may be obtained by the action of phosphorus pentachloride on camphoric acid,[5] and Walter prepared it by dissolving the acid in sulphuric acid and precipitating with water.[6] According to Maissen, an almost theoretical yield is obtained by boiling together equal molecules of acetic anhydride, anhydrous sodium acetate and

[1] *Jahresber. Chem.* 1862, 270; 1864, 402.
[2] Hartmann, *Ber. Deutsch. Chem. Ges.* xxi. 221.
[3] Loir, *Ann. Chim. Phys.* [3] xxxvii. 196.
[4] *Ibid.* lxiv. 152; *Ann. Chem. Pharm.* xxii. 32.
[5] *Ibid.* lxxxvii. 290.
[6] *Ann. Chim. Phys.* [3] ix. 177.

camphoric acid,[1] the same result being obtained by heating the latter with acetyl chloride :[2]



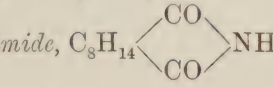
Several other methods of formation have already been mentioned. Camphoryl oxide is readily soluble in ether and crystallizes from alcohol in long needles or, on addition of benzene, in lustrous, rhombic prisms (Montgolfier). It melts at 216°—217°, boils above 270°, readily sublimes in needles and is gradually reconverted into the acid by boiling water.

Bromocamphoryl oxide, $C_{10}H_{13}BrO_3$. This substance, which is usually known as bromocamphoric anhydride, is formed when camphoryl oxide is heated with bromine.[3] It separates from chloroform in large, compact, rhombic crystals, which melt at 215°.

Camphoryl chloride, $C_{10}H_{14}O_2Cl_2$, is obtained by the action of two molecules of phosphorus pentachloride on one molecule of camphoric acid and is a yellowish liquid, which decomposes on heating and is gradually converted by water into camphoric acid.

Gaseous ammonia converts it into a viscid mass of *camphoramide*, $C_{10}H_{14}O_2(NH_2)_2$, which becomes crystalline after some time.[4]

Camphoramic acid, $C_8H_{14}(CO.NH_2)CO_2H$. When a boiling, concentrated alcoholic solution of the anhydride is saturated with ammonia, ammonium camphoramate crystallizes out on cooling. This salt is dissolved in water and decomposed with hydrochloric acid. The free acid thus obtained crystallizes in transparent, rectangular prisms.[5]

Camphorimide,  , was obtained by Laurent by heating ammonium camphoramate. It crystallizes from alcohol

[1] *Gaz. Chim. Ital.* x. 286.
[2] Anschütz, *Ber. Deutsch. Chem. Ges.* x. 1881.
[3] Wreden, *Ann. Chem. Pharm.* clxiii. 330 ; Fittig and Woringer, *ibid.* ccxxvii. 1.
[4] Moitessier, *ibid.* cxx. 252.
[5] Laurent, *ibid.* lx. 320.

in six-sided tablets, sublimes at 150° and melts, when heated in a sealed tube, at 180°.[1]

Camphorethylimide, $C_8H_{14}\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle N.C_2H_5$, is obtained by heating ethylamine camphorate and is a crystalline mass, which melts at 47°—48°, boils at 271°—273° and is converted by the action of phosphorus chloride into a crystalline chloride. This substance yields *camphorethylimidethylimidine* when acted upon by ethylamine:

$$C_8H_{14}\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right\rangle N.C_2H_5+H_2N.C_2H_5=C_8H_{14}\left\langle\begin{matrix}C{=}N.C_2H_5\\CO\end{matrix}\right\rangle N.C_2H_5+2HCl.$$

This is an oily liquid, which boils at 285°—286°, has a faint narcotic odour and bitter taste, and acts as a strong base. It is decomposed by hydrochloric acid at 200° into camphorethylimide and ethylamine.[2]

Paracamphoric acid is formed, as has been already stated, when concentrated solutions of dextro- and lævocamphoric acid are mixed; a rise of temperature takes place and the para-acid separates out on cooling. It is less soluble than its isomerides and is also formed by the oxidation of the inactive camphor, which occurs in oil of lavender.[3]

Mesocamphoric acid is obtained by heating camphoric acid to 140° with fuming hydrochloric acid[4] as well as, accompanied by paracamphoric acid, by heating it with water to 180°—220°.[5] It is more readily soluble in water than ordinary camphoric acid and crystallizes in soft, dull needles, which melt at 113°.

2526 *Camphanic acid*, $C_{10}H_{14}O_4$, was obtained by Wreden on treating camphoric anhydride with bromine and boiling the product with water.[6] Kachler shortly afterwards obtained it by heating campholic acid with moist bromine.[7] Wreden regarded it as hydroxycamphoric anhydride, but Fittig pointed out that it exhibits all the properties of a lactonic acid, the formation of which, in this case, can be readily understood, on the assumption

[1] Ballo, *Ann. Chem. Pharm.* cxcvii. 334.
[2] Wallach and Kamenski, *ibid.* ccxiv. 241.
[3] Chautard, *ibid.* cxxiv. 121.
[4] Wreden, *ibid.* clxiii. 327.
[5] Jungfleisch, *Ber. Deutsch. Chem. Ges.* vi. 680.
[6] *Ann. Chem. Pharm.* clxiii. 330.
[7] *Ibid.* clxii. 264.

that the brominated anhydride, which is the first product, is converted successively into bromocamphoric acid and hydroxycamphoric acid, the latter of which then passes into the lactone with elimination of water :[1]

$$C_8H_{13}\begin{cases}Br\\CO.OH\\CO.OH\end{cases} + H_2O = HBr + C_8H_{13}\begin{cases}OH\\CO.OH\\CO.OH\end{cases} =$$

$$C_8H_{13}\begin{cases}O\\|\\CO\\CO.OH\end{cases} + H_2O.$$

The accuracy of this view was soon proved by Rudzinsky-Rudno, who prepared salts of the dibasic hydroxycamphoric acid.[2]

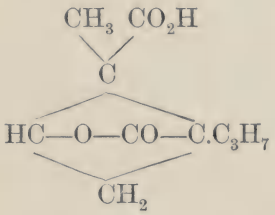
In order to prepare camphanic acid, 10 grms. of camphoric acid are heated to 120° with 12 grms. of bromine, until the colour of the latter has disappeared, and the product boiled with water. In order to remove any unaltered camphoric acid, the barium salts are prepared and purified by recrystallization.[3]

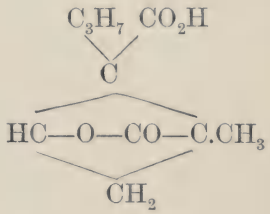
Camphanic acid is readily soluble in alcohol and ether ; it crystallizes from hot water in feathery forms or compact, monosymmetric prisms, melting at 200°.

Barium camphanate, $2(C_{10}H_{13}O_4)_2Ba + 7H_2O$, forms large crystals.

Ethyl camphanate, $C_{10}H_{13}O_4.C_2H_5$, is obtained by passing hydrochloric acid into an alcoholic solution of the acid, and crystallizes in thin prisms, which melt at 63° and readily sublime (Wreden).

The constitution of camphanic acid is expressed by one of the following formulæ :



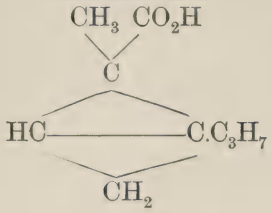


If it be submitted to dry distillation, it partially decomposes with evolution of carbon dioxide into two isomeric substances,

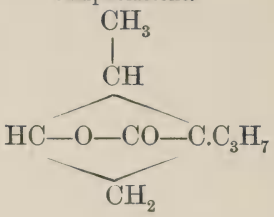
[1] *Ann. Chem. Pharm.* clxxii. 151.
[2] *Inauguraldiss.* Würzburg, 1879.
[3] Fittig and Woringer, *Ann. Chem. Pharm.* ccxxvii. 1.

the constitution of which, if the former of the above formulæ be assigned to camphanic acid, may be expressed as follows:

Lauronolic acid.



Campholactone.



Lauronolic acid, $C_9H_{14}O_2$, is also formed, together with the lactone, by heating barium camphanate to 200° with water. It is an oily liquid, which is tolerably soluble in cold, readily in hot water and ether. It is partially converted into the isomeric lactone by dilute hydrochloric acid in the cold, more rapidly on heating; the amount which undergoes this change never exceeds one half of the acid employed.

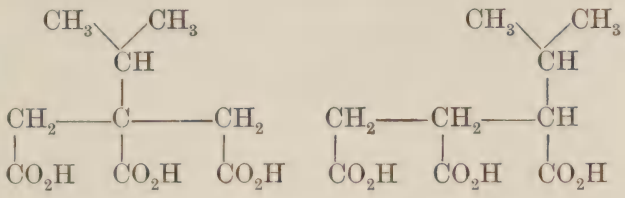
Calcium laurolonate, $(C_9H_{13}O_2)_2Ca + 3H_2O$, separates, when its solution is concentrated, in characteristic dendritic groups of small needles.

Campholactone, $C_9H_{14}O_2$, crystallizes in small, colourless needles, which have a characteristic smell, resembling that of camphor. It melts at 50° and boils at 230°—235°. Its aqueous solution becomes turbid on heating, owing to the separation of oily drops, but is again rendered clear by a further rise of temperature. The inverse change takes place on cooling. Alkalis dissolve the lactone with formation of the corresponding hydroxy-acid, which is precipitated by the addition of acids at 0°, as an oil, which solidifies in small needles and is readily reconverted into the lactone (Fittig and Woringer).

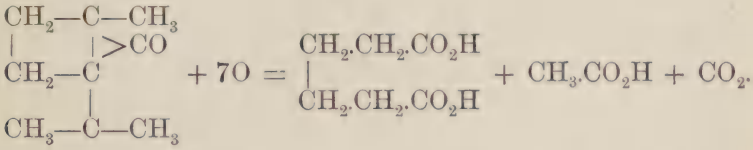
2527 *Camphoronic acid*, $C_9H_{14}O_6$, is an oxidation product of camphoric acid and occurs in considerable quantity in the mother-liquors obtained in the preparation of the latter. It is readily soluble in water and alcohol, and crystallizes in dazzling white, microscopic needles or small, vitreous prisms, which melt at 136°—137°, and decompose on distillation into water and the anhydride, $C_9H_{12}O_5$. The latter forms rhombic crystals and readily recombines with water to form the acid. This is tribasic and yields isobutyric acid on fusion with caustic potash.[1]

[1] Kachler, *Ann. Chem. Pharm.* clix. 286; clxii. 262; cxci. 143; Bredt, *ibid.* ccxxvi. 249.

It must therefore be considered as *isopropylcarballylic acid*, the formation of which from camphoric acid can readily be understood, and its constitution represented by one of the following formulæ:



Camphophorone, $C_9H_{14}O$. This substance was obtained by Gerhardt and Liès-Bodart [1] by the distillation of calcium camphorate and is also formed when camphor is heated to 100° with sulphuric acid.[2] It is a liquid which has an aromatic odour, boils at about 210° and is oxidized by chromic acid solution to acetic and adipic acids:[3]



This substance appears to be identical with the *isophorone* obtained, together with other products, by the distillation of cane [4] or grape-sugar [5] with lime, and which is also formed from glycerol by a fungoid fermentation and by passing glycerol over a mixture of lime and zinc dust at a low red heat.[6] The phorone, which is formed by heating acetone with lime [7] or sodium,[8] also appears to be camphophorone, while that which is obtained by the action of hydrochloric acid on acetone (Pt. I. p. 573) is certainly a different compound (Kachler).

Sulphocamphylic acid, $C_9H_{16}SO_6 + 2H_2O$. This remarkable compound was obtained by Walter by heating camphoric acid with sulphuric acid, camphoric anhydride being, as already

[1] *Ann. Chem. Pharm.* lxxii. 293.
[2] Chautard, *Jahresb. Chem.* 1857, 483; Schwanert, *Ann. Chem. Pharm.* cxxiii. 298.
[3] Kachler, *ibid.* clxiv. 79.
[4] Fremy, *ibid.* xv. 278; Benedikt, *ibid.* clxii. 303.
[5] Liès-Bodart, *ibid.* c. 353.
[6] Schulze, *Ber. Deutsch. Chem. Ges.* xv. 64.
[7] Fittig, *Ann. Chem. Pharm.* cx. 32; cxii. 309.
[8] Städeler, *ibid.* cxi. 279.

mentioned, the first product.[1] He named it *sulphocamphoric acid* and expressed its formation by the following equation:

$$C_{10}H_{16}O_4 + H_2SO_4 = C_9H_{16}SO_6 + CO + H_2O.$$

Dumas explained the course of the reaction by supposing that the sulphuric acid residue replaced an atom of carbon, which had combined with one atom of oxygen of the sulphuric acid (Pt. I. p. 14).

It is best prepared, according to Kachler, by dissolving camphoric anhydride in sulphuric acid, heating to 65° until no further evolution of carbonic oxide occurs and diluting with water. The solution is then extracted with ether, in order to remove camphoric and mesocamphoric acids, the excess of sulphuric acid neutralized with lead oxide, the filtrate treated with sulphuretted hydrogen and finally evaporated in a vacuum.[2]

Sulphocamphylic acid crystallizes in six-sided, asymmetric prisms,[3] which are readily soluble in water. It is a strong, dibasic acid, the constitution of which is still quite unknown. On fusion with potash, the compound $C_9H_{12}O_2$ is formed, and separates from alcohol in monosymmetric crystals, melting at 148°; it dissolves in alkalis and is reprecipitated without change by the addition of acids.

Damsky, who wished to investigate this substance, was unable to prepare it, but obtained an isomeric compound. This melts at 99° and is a well-defined acid, which forms crystallized salts and decomposes on distillation with soda lime into carbon dioxide and the hydrocarbon C_8H_{12}. The latter is a pleasantly-smelling liquid, which boils at 133°—135° and absorbs oxygen from the air, with formation of a viscid mass.[4]

LIMONENE GROUP.

2528 *Limonene*, $C_{10}H_{16}$, is, according to Wallach, a terpene, first found in the rind of the fruit of the Agrumi (oranges, lemons, &c.), and from which the following ethereal oils were prepared on the large scale by the Arabians as early as the sixteenth century, if not still earlier.

[1] *Ann. Chim. Phys.* [3] ix. 177.
[2] *Ann. Chem. Pharm.* clxix. 178.
[3] *Jahresb. Chem.* 1877, 642.
[4] *Ber. Deutsch. Chem. Ges.* xx. 2959.

Oil of lemon is prepared from the lemon, *Citrus limonum*. In Messina and Palermo the fresh rinds are pressed against a sponge, which receives the oil, and when saturated with it, is forcibly wrung by the workman, the contents being received in an earthen bowl. In Nice and Mentone the fresh fruit is rubbed over brass pins, which are fastened vertically in a vessel "*Ecuelle à piquer*," and the oil (*Essence de citron à zeste*) collected in a tube with which the bottom of the vessel communicates. This tedious hand work has been partially replaced by Monfalcone's "Strizzatore termopneumatico," driven by a small steam engine. This machine consists of a double-walled drum of sheet iron, which is rapidly rotated and thus forces the fruit against pins placed along the walls. An oil of poorer quality (*Essence de citron destillé*) is obtained by distilling the peel with water.

Oil of orange peel is prepared in the same way in Sicily and Southern France from the rind of the unripe fruit of *Citrus Bigaradia*, which yields the finest oil (*Essence de Bigarade*), while that obtained from *Citrus Aurantium* (*Essence de Portugal*) is less valuable.

Oil of bergamot, which is a highly-prized perfume, is obtained from the scarcely ripened fruit of *Citrus bergamia*, a tree which is cultivated near Reggio in Calabria. This perfume is first mentioned in the year 1688 in the inventory of an apothecary in Giessen.[1]

According to Tilden, oil of lemons contains as chief constituents lævopinene and *citrene*, accompanied by other substances. The latter is, as was found by Wallach, identical with *hesperidene*, the chief constituent of oil of orange peel. The same terpene, which he calls limonene, also occurs in oil of bergamot, oil of neroli, oil of nutmeg, oil of elder flowers, oil of pine needles, and oil of erigeron (*Erigeron canadense*). It is further identical with *carvene*, which occurs with carvol in oil of caraway and oil of dill. If these two be separated by fractional distillation and the adhering carvol then removed by means of phenylhydrazine, the carvene retains the characteristic odour of the seeds, which is however con-

[1] Further information about this oil may be found in Flückiger's *Pharmakognosie* and in *Pharmacographia* by Flückiger and Hanbury. It is stated in a small work *Le Parfumeur François*, par Le Sieur Barbe, parfumeur, 1693, that oil of bergamot is extracted from the fruit of a lemon, which has been grafted on a bergamot pear. The name of the latter is derived from the Turkish *beg-ârmâdî*, the prince of pears. Volkamer, in his *Hesperides Norimbergenses*, 1713, further describes *limon bergamotta* as "gloria limonum et fructus inter omnes nobilissimus," and mentions that the Italians prepare one of the finest essences from it.

verted into that of oil of lemon when the carvene is shaken up with potassium permanganate and dilute sulphuric acid.

Limonene has the sp. gr. of 0·846 at 20°, boils at 175°—177°, is dextrorotatory and is converted by heating to 250°—270° into dipentene, a portion being simultaneously polymerized; dipentene is also formed from it by the action of hydrochloric acid (p. 456).

Limonene tetrabromide, $C_{10}H_{16}Br_4$, is prepared from the terpene by diluting one volume of this with four of ether and four of alcohol, cooling with ice and gradually adding 0·7 volumes of bromine, care being taken not to allow the temperature to rise too high. The solution is then allowed to evaporate in a basin, when, if the hydrocarbon was pure, crystals soon separate out. The alcohol is added to keep the oily by-products, which are always formed, in solution, while the tetrabromide is almost insoluble in it. It is also readily formed by the addition of bromine to a solution of limonene in ten parts of glacial acetic acid, and separates in hemihedral, rhombic, soft and pliable crystals, which melt at 104°—105°,[1] and are more soluble in ether than dipentene bromide; the solution is also dextrorotatory.

Limonene nitrosochloride, $C_{10}H_{16}NOCl$, is obtained by passing nitrosyl chloride into a mixture of one part of oil of orange peel and five parts of methylated spirits, cooled to −10°. It thus forms a crystalline precipitate, which melts at 103° and is thus converted into carvoxime.[2]

2529 *Carvol*, $C_{10}H_{14}O$, occurs, as has already been mentioned, in oil of caraway (*Carum carvi*), together with limonene, from which it may be separated by fractional distillation.[3] In order to obtain it perfectly pure, the fraction of the oil which boils above 190° is treated with an equal volume of alcoholic ammonium sulphide; after some time the compound $(C_{10}H_{14}O)_2SH_2$ separates in long needles, which are decomposed by alcoholic caustic potash with separation of carvol.[4] It also occurs in oil of fennel (*Anethum foeniculum*)[5] and in oil of dill (*Anethum graveolens*). It is a liquid, which smells like caraway, boils at 224°—225°, and is dextrorotatory, while a laevorotatory carvol is obtained from the oil of mentha crispa.[6] Both of these

[1] Wallach, *Ann. Chem. Pharm.* ccxxvii. 277.
[2] *Journ. Chem. Soc.* xxxi. 558.
[3] Völkel, *Ann. Chem. Pharm.* lxxxv. 246.
[4] Varrentrapp, *Handwörterb.* iv. 686.
[5] Nietzki, *Neues Handwörterb.* ii. 986.
[6] Beyer, *Ber. Deutsch. Chem. Ges.* xvi. 1387; see also Flückiger, *ibid.* xvii. Ref. 358.

modifications are readily converted into the isomeric carvacrol (p. 454).

Carvoxime, $C_{10}H_{14}(N.OH)$, was first obtained by Tilden and Shenstone by heating limonene nitrosochloride, and was named by them nitrosohesperidine. It is more readily formed when the chloride is heated with alcohol, and is also obtained by the action of hydroxylamine on carvol. It crystallizes from alcohol in large, transparent tablets, which melt at 71° and are converted by heating with an alcoholic solution of sodium methylate and methyl iodide into the methyl ether, $C_{10}H_{14}(NOCH_3)$, which is a colourless liquid and has a smell resembling that of carrots.

The benzoyl ether, $C_{10}H_{14}(NO.CO.C_6H_5)$, is prepared by the action of benzoyl chloride; it crystallizes from hot petroleum-spirit in lustrous needles, melting at 95°.

Carvolhydrazone, $C_{10}H_{14}(N_2H.C_6H_5)$, crystallizes from alcohol in fine needles, melting at 216°.[1]

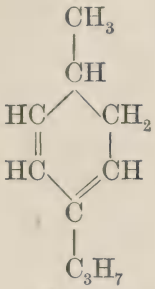
Hydrochlorocarvol, $C_{10}H_{15}ClO$, is formed, as observed by Varrentrapp, when hydrochloric acid passed into carvol, as an oily liquid. It is converted by hydroxylamine into *hydrochlorocarvoxime*, $C_{10}H_{15}Cl(NOH)$, which is also obtained by the combination of hydrochloric acid with carvoxime and crystallizes in tablets, melting at 132°. It is isomeric with limonene nitrosochloride, from which it differs by its solubility in cold caustic soda solution, in which the latter is quite insoluble. The nitrosochloride is also not attacked by benzoyl chloride, which readily converts hydrochlorocarvol into the benzoic ether, $C_{10}H_{15}Cl(NO.CO.C_6H_5)$, which crystallizes from petroleum-spirit in lustrous needles, melting at 114°—115°.[2]

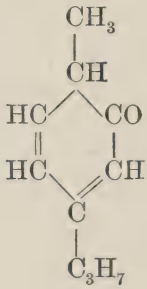
Carveol or *Carvyl alcohol*, $C_{10}H_{15}.OH$, is formed by the action of sodium on an alcoholic solution of carvol and is a somewhat viscous liquid, which has an odour different from that of carvol, boils at 218°—220, and is converted by acid chlorides into liquid ethers.[3]

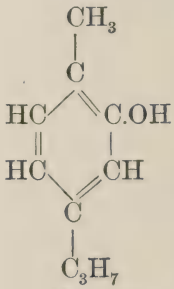
Carvylamine, $C_{10}H_{15}.NH_2$, is obtained by treating an alcoholic solution of carvoxime with glacial acetic acid and sodium amalgam. It is a liquid, which has an aromatic and ammoniacal odour, rapidly absorbs carbon dioxide from the air and forms a crystalline hydrochloride, which is converted by sodium nitrite into carveol (Goldschmidt and Kisser).

[1] Goldschmidt and Zürrer, *Ber. Deutsch. Chem. Ges.* xviii. 1729, 2220.
[2] Goldschmidt and Kisser, *ibid.* xx. 486. [3] Leuckart, *ibid.* xx. 114.

The constitution of the members of this group can readily be understood. Carvol is a ketone and stands in close relation to carvacrol or orthocymophenol. It is derived from limonene, which is a dihydrocymene, by the replacement of two atoms of hydrogen by one of oxygen. Both are optically active and therefore an asymmetric carbon atom must be present. The following formulæ are thus arrived at:


Limonene.

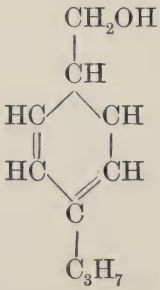

Carvol.


Carvacrol.

Hence carvacrol stands in the same relation to carvol as phloroglucinol to triketohexhydrobenzene, the latter being however unknown in the free state.

The fact that limonene contains two double linkings is also proved by its specific refraction.[1]

Anthemol or *Anthemyl alcohol*, $C_{10}H_{15}.OH$, occurs as the angelic or tiglic ether in cumin oil and is a thick liquid, which smells like camphor, boils at 213·5°—214·5° with slight decomposition and is oxidized by boiling dilute nitric acid to paratoluic and terephthalic acids.[2] It may perhaps be a derivative of limonene, and would in that case probably have the following constitution:



[1] Brühl, *Ber. Deutsch. Chem. Ges.* xxi. 145.
[2] Köbig, *Ann. Chem. Pharm.* cxcv. 92.

DIPENTENE GROUP.

2530 *Dipentene*, $C_{10}H_{16}$. Wallach and Brass, by the action of hydriodic acid on cineol, $C_{10}H_{18}O$, a substance which is mentioned below, obtained a di-iodide, $C_{10}H_{18}I_2$, which on heating with aniline yielded a terpene, which they termed *cynene*,[1] the name being changed by Wallach at a later date into *cinene*. This substance is identical with *cajeputene*, which is obtained by heating oil of cajeput with phosphorus pentoxide,[2] and also with Berthelot's *isoterebentene*, which is formed, together with polymerides, by heating oil of turpentine to 250°—270° and is obtained in a similar manner from all pinenes and from limonene, so that it is contained in Swedish and Russian oil of turpentine, which is prepared from pinewood-tar. It is further identical with caoutchin, obtained by the distillation of caoutchouc and gutta-percha. In addition to these substances, isoprene, C_5H_8, is formed by the same process and is converted by heat into a terpene, which was named *di-isopropene* or *terpilene*[3] and, as was shown by Wallach, is also cinene. The *divalerylene* obtained from valerylene, C_5H_8, is also probably identical with this hydrocarbon.[4] On account of this method of formation, the name of *dipentene* was given by Wallach to cinene.[5] It forms the chief constituent of the terpene, which Bauer and Verson obtained by heating rutylene dibromide, $C_{10}H_{18}Br_2$, with alcoholic potash[6] and of that which was prepared by Radziszewski and Schramm by converting the fraction of commercial amylene, which boils between 37°—39°, into the hydrochloride, $C_5H_{10}Cl(OH)$, heating this with ammonia and treating the hydroxyamylamine thus formed with phosphorus pentoxide:[7]

$$2C_5H_{10}(NH_2)OH = C_{10}H_{16} + 2NH_3 + 2H_2O.$$

Dipentene is also formed with elimination of water from terpine, $C_{10}H_{18}(OH)_2$, terpineol, $C_{10}H_{17}(OH)$ and cineol, $C_{10}H_{18}O$,

[1] *Ann. Chem. Pharm.* ccxxv. 299.
[2] Schmidt, *Jahresber. Chem.* 1860, 481.
[3] Tilden, *Journ. Chem. Soc.* xlv. 410; Bouchardat, *Compt. Rend.* lxxx. 1446; lxxxvii. 657; lxxxix. 361 and 1117.
[4] Bouchardat, *Bull. Soc. Chim.* xxxiii. 24.
[5] The hydrocarbons, C_5H_8, are however called pentines, while the name pentene is synonymous with pentylene or amylene.
[6] *Ann. Chem. Pharm.* cli. 52.
[7] *Ber. Deutsch. Chem. Ges.* xvii. 838.

which will be subsequently described. It is best prepared from its dihydrochloride, $C_{10}H_{15}Cl_2$, which is obtained by the action of hydrochloric acid on the compounds just mentioned or by direct combination with limonene or moist pinene. The chloride is boiled with one part of anhydrous sodium acetate and two parts of glacial acetic acid for half an hour in a flask provided with an inverted condenser, the product distilled with steam, boiled with caustic potash, redistilled, dried and finally purified by fractional distillation.[1]

Wallach detected it in considerable quantity in the ethereal oil of the camphor tree; this is the more remarkable as it has hitherto not been found in any other natural product. According to Brühl, however, it appears to occur in oil of cascarilla.

Dipentene and its derivatives are optically inactive; it boils at 180°—182°, has a pleasant odour of lemons and a sp. gr. of 0·8538 at 16°. On agitation with concentrated sulphuric acid, it is partially converted into a resin, sulphur dioxide is evolved and cymene separates out on the addition of water. This hydrocarbon is also formed when dipentene is heated with phosphorus pentachloride (Wallach and Brass), a reaction which supplies the explanation of previously conflicting statements. Völkel obtained cynene from oil of wormseed or impure cineol and purified it by means of sulphuric acid;[2] according to Gräbe, the same hydrocarbon is formed by the action of phosphorus pentasulphide on the oil,[3] while Faust and Homeyer stated that cymene is thus obtained.[4]

The latter is also formed by the action of concentrated sulphuric acid on oil of turpentine, this being first converted into dipentene, which is also obtained when oil of turpentine is boiled with alcoholic sulphuric acid, but is partially converted into terpines and other products if the boiling be continued for some time.

Dipentene tetrabromide, $C_{10}H_{16}Br_4$, was first obtained by Wallach and Brass from cineol; it is prepared from dipentene in a similar manner to limonene tetrabromide; like this it forms rhombic crystals, which, however, are less soluble in ether than those of the limonene derivative and always show the macrodome but never a hemihedral face. In addition to this,

[1] Wallach, *Ann. Chem. Pharm.* ccxxxix. 1.
[2] *Ibid.* lxxxix. 358.
[3] *Ber. Deutsch. Chem. Ges.* v. 680.
[4] *Ibid.* vii. 1429.

they melt at 125°—126°, are very brittle and show reed-like striations on faces of the vertical zone. Dipentene may be readily detected in mixtures by means of this characteristic compound.

2531 *Dipentenylene glycol*, $C_{10}H_{18}(OH)_2 + H_2O$. Geoffroy, in the year 1727, observed the presence of crystals in an old specimen of oil of turpentine, which were taken by Buchner for the succinic acid salt of a volatile base. Dumas and Peligot investigated the substance and found that this *oil of turpentine camphor* is a hydrate, $C_{10}H_{16} + 3H_2O$, and that it also occurs in basil-camphor (*Ocymum basilicum*) and the oil of *Elletaria cardamomum*.[1]

Wiggers then discovered a method for obtaining this interesting substance from turpentine in any wished for amount. "In the neighbourhood of Bremen a mixture of oil of turpentine, alcohol, nitric acid and an extremely small quantity of oil of sassafras is largely employed by veterinary surgeons. The occurrence of crystals in this mixture has been observed by Herr Martfeld, dispenser to an apothecary in Otterberg near Bremen, and in September 1839 he forwarded me a small portion for examination." These proved to be the so-called turpentine-camphor and are formed, as shown by Wiggers, in large quantities whenever a mixture of oil of turpentine, alcohol and nitric acid is allowed to stand;[2] a detailed account of the best method of preparation has also been given by the same author.[3] He found that one molecule of water is lost on fusion, and this is considered by List to be water of crystallization, since it is also lost over sulphuric acid. Since the other two molecules of water are more firmly combined, the name hydrate of oil of turpentine appeared to him to be inadmissible, and as that of turpentine-camphor was obviously unsuitable, he took advantage of the name terpine, which had been proposed by Berzelius, and termed the substance *terpine hydrate*.[4]

Deville then found that the same compound may also be obtained from oil of lemon and oil of bergamot.[5]

In order to prepare dipentenylene glycol, which is the most suitable name for this compound, eight parts of oil of turpentine are mixed with two parts of alcohol and two parts of nitric acid of sp. gr. 1·25—1·30 in flat basins.[6] After a few days the mother-

[1] *Ann. Chem. Pharm.* xiv. 75.
[2] *Ibid.* xxxiii. 358.
[3] *Ibid.* lvii. 247.
[4] *Ibid.* lxvii. 362.
[5] *Ibid.* lxxi. 348.
[6] Hempel, *ibid.* clxxx. 71.

liquor is poured off from the crystals, which have already separated and is neutralized with an alkali, after which treatment another crop of crystals separates out.[1] The preparation only succeeds at the cool seasons of the year, as in summer a resinous mass is usually obtained.[2] According to Tilden, one volume of nitric acid of sp. gr. 1·4 is mixed with one volume of strong alcohol and half a volume of rectified oil of turpentine, the mixture allowed to stand for two days, until all the smell of turpentine has vanished, and then poured into flat dishes, alcohol being added from time to time; about one-third of the oil of turpentine is thus converted into glycol and a still larger yield may be obtained by continuing the operation.[3] The American and French oils of turpentine may both be employed for its preparation, while it cannot be obtained from the terpenes of the various species of Citrus (Tilden).

Dipentenylene glycol crystallizes in large, transparent, monosymmetric prisms,[4] which dissolve in 200 parts of cold and 22 parts of boiling water[5] and are still more readily soluble in alcohol. When it is heated in a capillary tube, it commences to fuse above 100° and melts at 116°—117° to a clear liquid, the fusion being accompanied by frothing and the sublimation of a small portion of the substance into the cooler portion of the tube. On distillation, the water of crystallization is first lost and the anhydrous compound then boils at 258° and solidifies on cooling to a hard mass, melting at 102°, which is very hygroscopic and readily combines with water, but not with bromine.

2532 *Dipentenyl oxide* or *Cineol*, $C_{10}H_{18}O$, is the chief constituent of oil of wormseed.[6] When it is cooled by a freezing mixture and treated with hydrochloric acid, the compound $(C_{10}H_{18}O)_2HCl$, separates out in deliquescent crystals, which are decomposed by water. The pure compound is obtained by a repetition of this operation and is then distilled with water and heated with alcoholic potash to remove adhering hydrochloric acid, after which it is again distilled with steam.[7]

[1] Wallach, *Ann. Chem. Pharm.* ccxxvii. 284.
[2] *Ibid.* ccxxx. 248.
[3] *Journ. Chem. Soc.* xxxiii. 247. It is stated in *Jahresber. Chem.* 1878, 638, that Tilden used methyl alcohol, while he actually employed methylated spirits.
[4] Rammelsberg, *Pogg. Ann.* lxiii. 570.
[5] Blanchet and Sell, *Ann. Chem. Pharm.* vi. 268.
[6] Wormseed consists of the unexpanded flower-buds of *Artemisia maritima*, a shrub which is indigenous to South-Eastern Russia and Central Asia. Its name, *Semen cynae*, is derived from the Italian semenzina, the diminutive of semenza (seed), and is therefore more correctly written *Semen cinae* (Flückiger).
[7] Wallach and Brass, *Ann. Chem. Pharm.* ccxxv. 291.

Cineol is identical with *cajuputol*, which is the chief constituent of oil of cajeput,[1] and with *eucalyptol*,[2] and occurs in conjunction with ordinary camphor, $C_{10}H_{16}O$, and Borneo camphor, $C_{10}H_{18}O$, in oil of rosemary[3] and oil of spike,[4] this occurrence being especially remarkable because these three compounds had not previously been found together.

Cineol is a liquid, which has a pleasant smell, resembling that of camphor, is optically inactive, boils at 176°—177° and solidifies when at a low temperature to crystals, melting at − 1°; its sp. gr. at 16° is 0·923. When it is agitated with a concentrated solution of iodine in potassium iodide, a pasty mass is formed containing greenish, lustrous plates, which after drying on a porous plate rapidly deliquesce.[5] The presence of cineol in oil of rosemary may be detected by this reaction (Weber).

Cineol also combines with hydrobromic and hydriodic acids, and is converted by the continued action of the latter into dipentenylene iodide. It unites with bromine to form *cineol dibromide*, $C_{10}H_{18}Br_2O$, which crystallizes in red needles or prisms, and readily decomposes into water, bromine and dipentene, one half of this last combining with the bromine to form the tetrabromide. It combines with iodine to form the compound, $C_{10}H_{18}I_2O$, crystallizing from petroleum-spirit in long, dark needles, which are more stable than those of the bromide.

If cineol be heated with alcoholic sulphuric acid, it is converted into terpinene and terpinolene.[6] It is not attacked by sodium, nor by benzoyl chloride below 120°, while above this temperature hydrochloric acid, dipentene and benzaldehyde are formed. It does not combine with hydroxylamine and phenylhydrazine. It is therefore neither a ketone nor an alcohol, but appears to stand in the same relation to dipentenylene glycol as ethylene oxide to its glycol.

[1] Wallach, *Ann. Chem. Pharm.* ccxxv. 316. Oil of cajeput is obtained in the Dutch East-Indian Island Bouro by the distillation of the leaves of the Kayuputi (the white-wood tree, *Melaleuca Leucadendron*) and is first mentioned by Rumphius. It became known in Germany at the commencement of the eighteenth century and was quoted in the tariffs of several apothecaries, while it was first employed in England in the present century (Flückiger and Hanbury).

[2] Jahns, *Ber. Deutsch. Chem. Ges.* xvii. 294. Eucalyptol is the chief constituent of the ethereal oil of *Eucalyptus globulus* and probably also of *E. oleosa*. These oils are imported from Australia and are chiefly employed for the adulteration of other ethereal oils, but have also a limited application for medicinal purposes.

[3] Weber, *Ann. Chem. Pharm.* ccxxxviii. 90.

[4] Voiry and Bouchardat, *Compt. Rend.* cvi. 351.

[5] Kraut and Wahlfors, *Ann. Chem. Pharm.* cxxviii. 294.

[6] Wallach, *ibid.* ccxxxix. 22.

2533 *Dipentenylene chloride* or *Terpene dihydrochloride*, $C_{10}H_{18}Cl_2$. Thenard observed that oil of lemon combines with hydrochloric acid. The compound thus obtained was investigated by Blanchet and Sell, who described it as *hydrochloride of oil of lemon*,[1] while Dumas named it *camphor of oil of lemon*.[2] List then obtained *terpine hydrochloride* by the action of hydrochloric acid on terpine hydrate, and stated that it is isomeric with oil of lemon camphor,[3] while Deville contended that the two substances are identical.[4] Oppenheim found that the same compound is formed when terpine is treated with the chlorides of phosphorus,[5] and Berthelot then observed that it may also be obtained by allowing oil of turpentine to stand in contact with concentrated hydrochloric acid for a month or by saturating a solution of the oil in alcohol, ether or acetic acid with hydrochloric acid. Pinene hydrochloride is also formed by the last method,[6] but not when alcohol is employed (Flawitzky).[7]

Berthelot also stated that the chlorides obtained from oil of turpentine and oil of lemon are identical, and this was confirmed by Tilden, who found that the same chloride is also formed from many other terpenes.[8] These are first converted, as was shown by Wallach, into dipentene, which readily forms the chloride when hydrochloric acid is passed into its ethereal solution,[9] or more simply when a saturated solution of hydrochloric acid in glacial acetic acid is brought into contact with a solution of dipentene or limonene in acetic acid.[10] It crystallizes in rhombic tablets, which melt at 49°—50°, and passes into the glycol when it is allowed to remain in contact with dilute alcohol.[11] It has already been mentioned that a mixture of this hydrochloride with pinyl chloride forms a mixture of low melting point; such a mixture containing equal parts of the two compounds is liquid at the ordinary temperature and only solidifies at the freezing point of water.

It is readily soluble in alcohol, but separates out as an oil when the solution is heated. According to early statements, oil of lemon sometimes yields a liquid instead of a solid chloride by the action of hydrochloric acid. This admits of a simple

[1] *Ann. Chem. Pharm.* vi. 282.
[2] *Ibid.* ix. 61.
[3] *Ibid.* lxvii. 362.
[4] *Ibid.* lxxi. 351.
[5] *Bull. Soc. Chim.* iv. 85.
[6] *Ann. Chem. Pharm.* lxxxiv. 350.
[7] *Beilstein's Handbuch*, 1773.
[8] *Ber. Deutsch. Chem. Ges.* xii. 1131.
[9] *Ann. Chem. Pharm.* ccxxvii. 294 &c.
[10] Wallach, *ibid.* ccxxxix. 3.
[11] Flawitsky, *Ber. Deutsch. Chem. Ges.* xii. 2358.

explanation, since dipentenylene chloride is partially converted into terpinene by heating with alcohol or water, and the liquid chloride of this is an excellent solvent of the solid compound (Wallach).

When dipentenylene chloride is heated with a trace of ferric chloride, it becomes coloured a bright violet and finally blue.[1]

Dipentenylene bromide, $C_{10}H_{18}Br_2$, was obtained by Oppenheim in an impure state by the action of phosphorus tribromide on the glycol, whilst Hell and Ritter prepared it by passing hydrobromic acid into well-cooled oil of wormseed.[2] It is best prepared by saturating glacial acetic acid with hydrobromic acid and adding a solution of limonene or dipentene in glacial acetic acid, the bromide separating out immediately. It is also formed when the glycol is agitated with hydrobromic acid (Wallach). It resembles the chloride very closely and melts at 64°.

Dipentenylene iodide, $C_{10}H_{18}I_2$, was also obtained by Oppenheim in an impure state by the action of phosphorus tri-iodide on the glycol, and was prepared by Wallach and Brass, as already mentioned, from cineol and hydriodic acid. It is also readily formed when the glycol is agitated with concentrated hydriodic acid[3] and when limonene or dipentene are treated with hydriodic acid in acetic acid solution.[4] It decomposes with great readiness, but becomes more stable as its purity increases. It crystallizes from petroleum-spirit in transparent rhombic prisms, which melt at 77°, or sometimes in monosymmetric tablets, melting at 78°—79°. It changes when kept for some time, more rapidly when heated, into a deep brown liquid, the formation of which may be much delayed by preserving it under water in which a piece of phosphorus is placed.

2534 *Terpineol* or *Dipentenyl alcohol*, $C_{10}H_{17}.OH$. Wiggers, by the action of hydriodic acid on terpine hydrate, obtained the compound $2C_{10}H_{16} + H_2O$, which was investigated by List and named *terpinol*.[5] It is also formed when terpine hydrate is boiled with hydrochloric acid, very dilute sulphuric acid, potassium sulphate, &c., and is a colourless, strongly refractive liquid, which boils at 168° and, especially when diluted, has a pleasant smell of hyacinths. Oppenheim was unable to obtain

[1] Riban, *Ann. Chim. Phys.* [5] vi. 37.
[2] *Ber. Deutsch. Chem. Ges.* xvii. 2609.
[3] Wallach, *Ann. Chem. Pharm.* ccxxx. 249.
[4] *Ibid.* ccxxxix. 3 and 13.
[5] *Ibid.* lxvii. 367.

this compound of a constant boiling point,[1] and Tilden found that the above reaction yields a mixture of a terpene with a compound, $C_{10}H_{18}O$, for which he retained the name terpinol.[2] It is also formed, together with terpilene, when dipentenylene chloride is heated with water.

Wallach then showed that when the glycol is boiled with dilute sulphuric acid or phosphoric acid, the product consists, according to the conditions of the experiment, of dipentene, terpinolene, terpinene, cineol and the isomeric *terpineol*, this name being substituted for terpinol in order to correspond with borneol and cineol. It is formed by simple elimination of water from the glycol and is then partially converted into the other substances, as will be subsequently explained.[4]

In order to prepare it, 25 grms. of the glycol are boiled with 50 cb. cms. of aqueous phosphoric acid. It is a very thick liquid, which has a pleasant smell, is optically inactive and boils at 215°—218°. According to Bouchardat and Voiry,[5] it is also formed when the glycol is heated with very dilute sulphuric acid and solidifies at $-50°$ to crystals,[6] melting at 30°—32°, by the aid of which crystallization may be induced at the ordinary temperature. This compound was probably obtained by Deville as a by-product of the preparation of terpine hydrate,[7] and it also appears to occur in oil of cardamom from Ceylon (*Elletaria major*). Dipentenylene[8] chloride is formed when hydrochloric acid is passed into its ethereal solution:

$$C_{10}H_{17}.OH + ClH = C_{10}H_{18}\begin{matrix}OH\\Cl\end{matrix}$$

$$C_{10}H_{18}\begin{matrix}OH\\Cl\end{matrix} + ClH = C_{10}H_{18}\begin{matrix}Cl\\Cl\end{matrix} + H_2O.$$

It is converted by hydriodic acid into the iodide and combines with water, in presence of dilute hydrochloric acid, to form the glycol. It also combines with bromine, but the compound formed does not admit of purification; an excess of bromine converts it into dipentene tetrabromide. On heating with

[1] Wallach, *Ann. Chem. Pharm.* cxxix. 155.
[2] *Journ. Chem. Soc.* xxxiii. 247; xxxv. 287.
[3] Tilden, *Ber. Deutsch. Chem. Ges.* xii. 1132; see also Flawitzky, *ibid.* 857.
[4] *Ann. Chem. Pharm.* ccxxx. 241; ccxxxix. 20.
[5] *Compt. Rend.* civ. 996.
[6] Bouchardat and Lafont, *ibid.* cii. 1555.
[7] *Ann. Chem. Pharm.* lxxi. 351.
[8] Weber, *ibid.* ccxxxviii. 98.

sodium, hydrogen is evolved, and it decomposes when heated alone to 200° into water and dipentene, while it is partially converted by continued boiling with phosphoric acid into cineol and partially into terpinolene. Dilute sulphuric acid on the other hand produces chiefly terpinene.

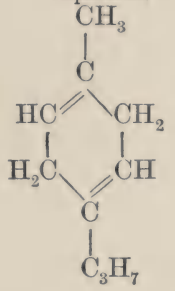
Dipentenyl phenylcarbamate, $C_{10}H_{17}O.CO.NH(C_6H_5)$, is formed by the combination of terpineol with phenyl carbimide and crystallizes from alcohol in long needles, melting at 110°.

Dipentenyl acetate, $C_{10}H_{17}O.CO.CH_3$ is obtained with difficulty when dipentene is heated with glacial acetic acid. It boils with decomposition at 220°, has an aromatic odour and is saponified by alcoholic potash with formation of terpineol (Bouchardat and Lafont).

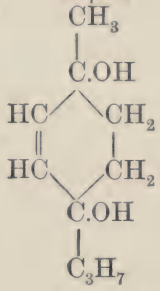
It follows from these facts that terpineol stands in the same relation to dipentenylene glycol as allyl alcohol to propylene glycol.

Dipentene is readily formed from limonene; like this it combines with four atoms of bromine, but differs from it in being optically inactive, as is also cineol, which is believed by Brühl to contain no double linkings.[1] These facts and the general behaviour of dipentene and its derivatives lead to the following constitutional formulae:

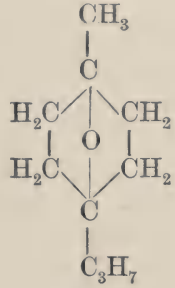
Dipentene.



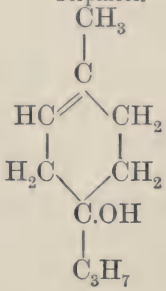
Terpine.



Cineol.



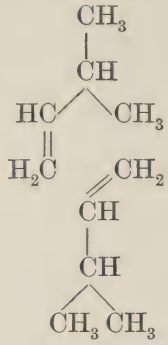
Terpineol.



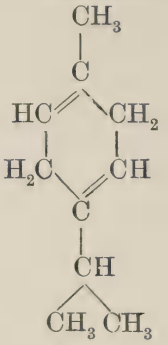
[1] Brühl, *Ber. Deutsch. Chem. Ges.* xxi. 460.

The formation of dipentene from amylene, &c., is also easily explained:

Amylene.



Dipentene.



According to this formula it would contain the isopropyl group, but this is known to pass very readily into the normal group.

SYLVESTRENE GROUP.

2535 Stockholm tar and Archangel tar are obtained in the North of Europe by the dry distillation of fir wood (*Pinus sylvestris* and *P. Ledbourii*), and these are the source of both Swedish and Russian turpentine. The former was found by Atterberg to contain both australene and sylvestrene,[1] which are stated by Tilden to be also present in Russian turpentine,[2] while Wallach has observed the occurrence of dipentene in addition to these.

Sylvestrene, $C_{10}H_{16}$, boils at 173°—175° (Atterberg) and smells like fresh fir wood; the chloride is formed by passing hydrochloric acid into its ethereal solution and yields the pure hydrocarbon on heating with aniline or better with sodium acetate and glacial acetic acid. In the pure condition it boils at 175°—178° and smells like oil of bergamot. The addition of a drop of concentrated sulphuric acid or fuming nitric acid to its solution in glacial acetic acid, or acetic anhydride, produces a splendid deep blue colouration. On heating to 250° it is partially polymerized, no dipentene or other terpene being formed, and it behaves in a similar manner towards boiling alcohol

[1] *Ber. Deutsch. Chem. Ges.* x. 1202. [2] *Journ. Chem. Soc.* xxxiii. 80.

containing sulphuric acid. It is dextrorotatory and combines with the hydracids to form compounds from which it can be separated unaltered.[1]

Sylvestrene tetrabromide, $C_{10}H_{16}Br_4$, is obtained by the addition of bromine to a solution of the hydrocarbon in glacial acetic acid. It crystallizes in monosymmetric tablets, melting at 135°—136°. Its ethereal solution is dextrorotatory.

Sylvestrenylene chloride, $C_{10}H_{18}Cl_2$. This compound, which is employed for the preparation of the pure hydrocarbon, is difficult to prepare from crude sylvestrene, since it is very soluble in the other hydrocarbons which are present. The separation must therefore be carried out at a low temperature, a mixture of the chloride with dipentenylene chloride being thus obtained, which is then separated by recrystallization from alcohol and ether. It crystallizes in long, hard, thin monosymmetric tablets, which melt at 72°, while a mixture with an equal amount of dipentenylene chloride fuses below 40°.

Sylvestrenylene bromide, $C_{10}H_{18}Br_2$, is prepared in a similar manner to the analogous dibromides; it resembles the chloride in every particular and melts at exactly the same temperature.

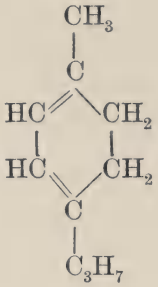
Sylvestrenylene iodide, $C_{10}H_{18}I_2$, crystallizes from hot petroleum-spirit in small plates, which melt at 66°—67° and readily become coloured brown.

TERPINOLENE GROUP.

2536 *Terpinolene* $C_{10}H_{16}$. The formation of this hydrocarbon has already been discussed. It is best prepared by boiling dipentenyleneglycol with four times its weight of aqueous phosphoric acid of 20 per cent.[2] It is formed in considerable quantity when sulphuric acid acts on cineol, much terpinene being also formed, which is then probably converted into terpinolene.[3] It boils at 185°—190° and is optically inactive. It combines with hydrochloric and hydrobromic acids to form the corresponding dipentene derivatives, resembling limonene

[1] Wallach, *Ann. Chem. Pharm.* ccxxx. 240; ccxxxix. 24.
[2] *Ibid.* ccxxx. 262.
[3] *Ibid.* ccxxxix. 23.

in this respect and in forming a distinctive tetrabromide. Brühl ascribes to it the following constitution :



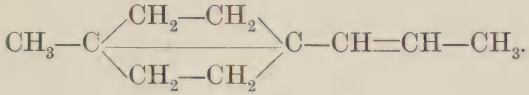
Terpinolene tetrabromide, $C_{10}H_{16}Br_4$, crystallizes from ether in very lustrous monosymmetric tablets, which melt at 116° and change on preservation into a porcelain-like mass, which commences to melt below 100°, the liquid assuming a green colour and gas being evolved. Crystals of the bromide may be re-obtained by extracting the cooled mass with ether, but the greater portion of it is destroyed.

TERPINENE GROUP.

2537 *Terpinene*, $C_{10}H_{16}$. The formation of this substance has frequently been referred to; it is formed by the action of sulphuric acid on pinene, dipentene, the glycol of the latter, cineol and phellandrene. In order to prepare it, 70 ccm. of concentrated sulphuric acid are added to two litres of oil of turpentine in portions of 5 ccm. at once, and the liquid well agitated, care being taken that the temperature does not rise so high that the vessel can no longer be conveniently handled. The mixture is then shaken up at repeated intervals for a whole day, neutralized with caustic soda and the product distilled with steam. Pure terpinene is obtained by fractional distillation of the product as a liquid, which boils at about 180° and smells like lemons.[1] It occurs also in oil of cardamom from Ceylon (*Elettaria major*),[2] is optically inactive and forms liquid addition-products with bromine and the hydracids;

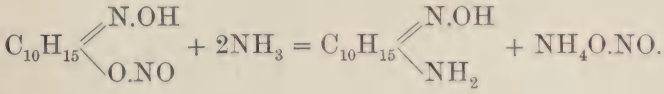
[1] Wallach, *Ann. Chem. Pharm.* ccxxx. 260; ccxxxix. 33.
[2] Weber, *ibid.* ccxxx. 98.

the hydrochloride, however, solidifies at a very low temperature. Dipentenylene chloride, which perhaps owes its formation to the presence of an impurity, is always formed together with the hydrochloride. It soon becomes resinous on exposure to air, and this change is also brought about to some extent by sulphuric acid, an isomeric terpene being also formed. It has probably the following constitution (Brühl):



Terpinene nitrosite, $C_{10}H_{16}N_2O_3$, is formed by the action of sodium nitrite and dilute acetic acid on terpinene and crystallizes from alcohol in snow-white, monosymmetric prisms, melting at 155°. It dissolves without decomposition in strong acids but is decomposed by boiling with alkalis.

Terpinene nitrolamine, $C_{10}H_{18}N_2O$, is obtained by the addition of ammonia to a hot alcoholic solution of the nitrosite:



It crystallizes from hot water in needles, which are readily soluble in alcohol and alkalis and melt at 116°—118°. Hydrochloric acid precipitates crystals of $C_{10}H_{18}N_2O.HCl$ from its ethereal solution. The amines react in a similar manner to ammonia, producing compounds most of which crystallize well.

Terpinene nitrolmethylamine, $C_{10}H_{15}(NH.CH_3)N.OH$, crystallizes from alcohol in splendid prisms, which melt at 141° and also form a crystalline hydrochloride.

Terpinene nitroldimethylamine, $C_{10}H_{15}N(CH_3)_2N.OH$, crystallizes less readily and melts at 160°—161°.

Wallach has prepared several additional compounds.[1]

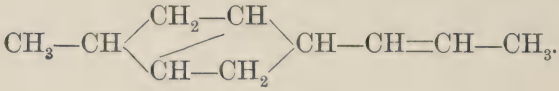
PHELLANDRENE GROUP.

2538 *Phellandrene*, $C_{10}H_{16}$. Cahours, who examined bitter

[1] *Ann. Chem. Pharm.* ccxli. 315.

fennel oil,[1] found in it, together with anethol, "a compound apparently isomeric with oil of turpentine," which is converted by nitrogen dioxide into a white crystalline substance. This latter, to be afterwards described, proved to be a compound of a terpene with nitrogen trioxide. Pesci submitted the ethereal oil of the seeds of the Water-Dropwort (*Phellandrium aquaticum*) to investigation and found in it the hydrocarbon phellandrene,[2] which was proved by Wallach to be identical with the terpene contained in bitter fennel oil.[3] It has not yet been obtained in the pure state; it boils at about 171°—172° and is dextrorotatory. Hydrobromic acid acts upon its solution in glacial acetic acid with production of a heavy, oily bromine compound, which is converted into dipentene by heating with sodium acetate and acetic acid, whilst terpinene is formed when it is treated with hot alcoholic sulphuric acid.

Brühl gives it the following constitution:



Phellandrene nitrosonitrite, $C_{10}H_{16}(NO)NO_2$. This compound, discovered by Cahours, was proved by Bunge not to be formed by the action of pure nitrogen dioxide on the hydrocarbon, but only in the presence of air. It is, therefore, more readily obtained by agitating the terpene with a solution of potassium nitrite and acetic acid.[4] It crystallizes in long needles, melting at 94° (Pesci) and is lævorotatory. Its solution in chloroform does not decolorize bromine, so that it behaves as a saturated compound. Its constitution is different from that of terpinene-nitrosite, since it is not converted into a nitrol-base by the action of amines (Wallach).

Phellandrene diamine, $C_{10}H_{16}(NH_2)_2$, was obtained by Pesci by the reduction of the preceding compound as a liquid, boiling at 209°—214°.

Nitrophellandrene, $C_{10}H_{15}NO_2$, is formed by the action of ammonia on nitronitrosophellandrene and is a yellow, aromatic

[1] The bitter fennel (*Fenouil amer*) is a variety of the ordinary fennel (*Anethum fœniculum*) which grows wild in Southern France, and whose seeds, which contain the oil, have an aromatic taste, resembling that of fennel, but taste bitter.

[2] *Gaz. Chim. Ital.* xvi. 225. [3] *Ann. Chem. Pharm.* ccxxxix. 40.

[4] *Zeitschr. Chem.* 1869, 579.

smelling liquid, which is converted by reduction into *amido-phellandrene*, $C_{10}H_{15}NH_2$, an oily liquid, which smells of coniine and forms crystalline salts.

COMPOUNDS RELATED TO THE CAMPHORS.

2539 *Menthol* or *Menthyl alcohol*, $C_{10}H_{19}.OH$, occurs, together with terpenes, in oil of peppermint, which is used in medicine, perfumery and for flavouring purposes. The peppermint (*Mentha piperita*) has been cultivated since the middle of last century at Mitcham in Surrey, near Wisbeach in Cambridgeshire, Market-Deeping in Lincolnshire, and Hitchin in Hertfordshire, and the oil extracted from the plants grown in those districts is still the most highly prized. Its culture has spread from England to other parts of Europe and to North America, whence considerable quantities of oil of peppermint are now obtained. Gaubius, in the year 1771, was the first to observe that the oil extracted from the plants near Utrecht deposited crystals of *Camphora Europaea Menthæ Piperitides*.[1] The Japanese and Chinese oils contain this substance in much larger quantities, and frequently occur in the form of a crystalline mass saturated with liquid hydrocarbons; these oils are not derived from the European peppermint, but from other species of Mentha (*M. arvensis var. piperascens et glabrata*).

This peppermint-camphor was mistaken for ordinary camphor until Dumas[2] and Blanchet and Sell[3] determined its composition, and Walter[4] fixed its molecular formula by a determination of its vapour density, which was found to be 5·62. It was recognized as an alcohol by Oppenheim.[5]

Menthol crystallizes in prisms, which have a strong smell of peppermint and melt at 42°.[6] It boils at 212°, is lævorotatory and decomposes on heating with phosphorus pentachloride or zinc chloride into water and *menthene*, $C_{10}H_{18}$, a dextrorotatory liquid, which smells like cymene, boils at 167° and combines with bromine. The addition product, $C_{10}H_{18}Br_4$ thus formed is converted into cymene by heating and distilling the product with sodium (Beckett and Wright).

[1] Flückiger, *Pharmakognosie*, 686.
[2] *Ann. Chem. Pharm.* vi. 252.
[3] *Ibid.* vi. 293.
[4] *Ibid.* xxxii. 288.
[5] *Ibid.* cxx. 350; cxxx. 176.
[6] Beckett and Wright, *Journ. Chem. Soc.* 1876, i. 1.

Menthol is employed both for internal and external application in medicine, and is sold in pencils as a remedy for neuralgia. The Chinese peppermint oil serves the same purpose and has long been employed in this way in China and Japan, where it is sold in small bottles under the name of *Po-ho-yo*.

Sodium menthylate, $C_{10}H_{19}ONa$, forms a vitreous mass, which is readily soluble in alcohol.

Menthyl chloride, $C_{10}H_{19}Cl$, was obtained by Walter by the action of phosphorus pentachloride on menthol, while Oppenheim prepared it by heating with hydrochloric acid. It is also formed by the combination of menthene with hydrochloric acid and is a liquid, which has a pleasant odour resembling that of mace and a refreshing taste, and boils with decomposition at 204°.

Menthyl bromide, $C_{10}H_{19}Br$, is formed by the action of phosphorus bromide on menthol, and is a liquid which decomposes on boiling.

Menthyl iodide, $C_{10}H_{19}I$, forms a heavy, faintly yellow liquid, which, like the bromide, decomposes when heated with alcoholic potassium sulphide or ammonia, with formation of menthene.

Menthyl carbonate, $(C_{10}H_{19})_2CO_3$, is obtained, together with the following compound, when cyanogen is passed into a solution of sodium menthylate in toluene and the product treated with water. It is a crystalline mass which melts at 105°.

Menthyl carbamate, $C_{10}H_{19}O.CO.NH_2$, crystallizes from alcohol in thin prisms, which melt at 165° and readily sublime.[1]

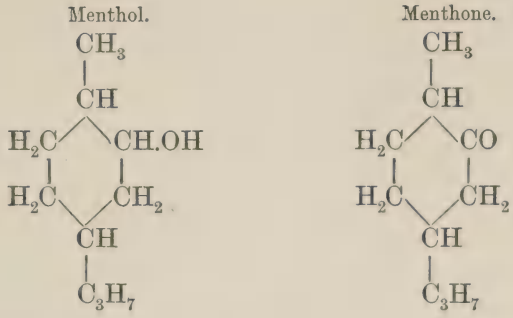
Menthyl phenylcarbamate, $C_{10}H_{19}O.CO.NH(C_6H_5)$, is formed by the combination of menthol with phenylcarbimide, and crystallizes from alcohol in silky needles, melting at 111°.[2]

Menthyl acetate, $C_{10}H_{19}O.C_2H_3O$, was prepared by Oppenheim by heating menthol to 150° with glacial acetic acid or acetic anhydride as a thick, strongly refractive liquid, which is lævorotatory and boils at 222°—224°.

Menthone, $C_{10}H_{18}O$, is formed by heating menthol with sulphuric acid and potassium bichromate.[3] It is a mobile liquid, which smells of peppermint and boils at 206°. When its solution in petroleum is heated with sodium and a current of carbon dioxide passed through the mixture, the product yields menthol on decomposition with water. The latter substance

[1] Arth, *Compt. Rend.* xciv. 872.
[2] Leuckart, *Ber. Deutsch. Chem. Ges.* xx. 114.
[3] Moriya, *Journ. Chem. Soc.* 1881, i. 77.

therefore bears the same relation to menthone as borneol to camphor :[1]



The molecular refractions of the compounds also agree with these formulæ.[2]

ISOMERIDES OF BORNEOL.

2540 The genus *Andropogon* is distinguished from other grasses by the fact that many of its species contain an essential oil, which is employed in India as a perfume and as a medicine and is also valued in Europe for its fragrance.

Indian Melissa oil or *Lemon-grass oil* is derived from *A. citratus*, a lofty grass, which is cultivated in Singapore and Ceylon. It occurs in commerce under the name of *oil of verbena*, since its odour resembles that of the fragrant verbena (*Lippia citriodora*).

Citronella oil is extracted in the same districts from *A. nardus*, and smells like roses and lemons. It contains *citronellol*, $C_{10}H_{18}O$, which boils at about 210° and yields a dibromide, which decomposes on heating into water, hydrobromic acid and cymene.[3]

Indian oil of geranium is contained in *A. Schoenanthus*, a graceful grass indigenous to Northern and Central India. It is also called *Rúsa oil* and *oil of ginger grass*, and is exported in considerable quantities from Bombay to Europe, chiefly to

[1] Atkinson and Yoshida, *Journ. Chem. Soc.* 1882, i. 49.
[2] Brühl, *Ber. Deutsch. Chem. Ges.* xxi. 457.
[3] Gladstone, *Journ. Chem. Soc.* 1872, 7 ; Wright, *ibid.* 1874, 317.

Constantinople and Kazalanik, where it is used to adulterate attar of roses. In order to fit it for this purpose, it is exposed to the sun in flat basins, under which conditions it loses its somewhat acrid smell, which then becomes very similar to attar of roses.[1] It contains valerianic acid and *geraniol*, which will subsequently be further investigated.

Turkish oil of geranium is derived from *A. pachnodes*, indigenous to India, Persia and Arabia.

German oil of geranium, as well as the French *Oleum palmæ rosæ*, is obtained by the distillation of *Pelargonium Radula*, and contains *geraniol* and pelargonic acid [2] (Vol. III. Part I. p. 660). The oil prepared in Algiers from *P. roseum et odoratissimum* is very similar to these (Gintl).

Geraniol, $C_{10}H_{17}.OH$, can be separated from Indian oil of geranium as a colourless, strongly refractive liquid, which is optically inactive, boils at 232°—233°, and has a very pleasant smell of roses. It is oxidized by potassium permanganate to valerianic acid and is converted by heating with nitric acid into oxalic acid, nitrobenzene and other substances.

Geranyl ether, $(C_{10}H_{17})_2O$, is formed when the chloride is heated with water or to 100°—200° with geraniol, and is a liquid, which has a characteristic smell of peppermint and boils at 187°—190°.

Geranyl chloride, $C_{10}H_{17}Cl$, is obtained by the action of hydrochloric acid on geraniol, and is an oily liquid, which has an odour resembling that of camphor and decomposes on heating. *Geranyl bromide* and *iodide* may be prepared from this by the action of potassium bromide and iodide; they are heavy, oily liquids, which decompose even more readily than the chloride. The valerate, benzoate and cinnamate, have all been prepared and are pleasant smelling liquids, which cannot be distilled without decomposition.

Geranyl sulphide, $(C_{10}H_{17})_2S$, is formed by the action of the chloride on an alcoholic solution of potassium sulphide. It is a yellowish, very unpleasant smelling liquid.[3]

Linaloëol, $C_{16}H_{18}O$. Among the costly spices mentioned in the Old Testament is aloes, by which is to be understood not the sap of the aloe plant but the fragrant wood of *Aquillaria Agallocha*, a large forest-tree, a native of the Malay Peninsula and the neighbouring islands.

[1] *Pharmacographia*, 725; Flückiger, *Pharmakognosie*, 157.
[2] Gintl, *Jahresber. Chem.* 1879, 941.
[3] Jacobsen, *Ann. Chem. Pharm.* clvii. 232.

Lignum aloes was found up to the end of last century among our drugs, but is now exclusively employed in Eastern Asia as a perfume. Since the seventeenth century, a fragrant wood has been imported from Mexico to which the above name has been given, while *linaloes wood* now comes from Cayenne and is derived from *Icica altissima*. The linaloëol, contained in it, is a liquid, smelling of roses and lemons and boiling at 198°. It is converted by hydrochloric acid into a liquid chloride, $C_{10}H_{18}Cl_2$, which smells like camphor and on distillation with lime yields a terpene, having a characteristic, faintly aromatic odour and boiling at 168°—172°.[1]

Coriandrol, $C_{10}H_{18}O$, is the chief constituent of oil of coriander (*Coriandrum sativum*) and is a liquid, which volatilizes without decomposition only below 150°. If it be gradually heated, it commences to boil at this temperature, but the boiling-point rises, water being gradually eliminated and coriandryl ether, $(C_{10}H_{17})_2O$, formed. This substance boils at 168°—170° and is accompanied by a polymeric condensation product, boiling at 190°—196°. When coriandrol is heated to 200° or distilled over phosphorus pentoxide, a terpene is obtained, together with polyterpenes. Coriander oil detonates very violently with iodine; the first product of the action of potassium permanganate upon it is an oily liquid, boiling at 185°—186°, which is isomeric with camphor and is converted into carbon dioxide, acetic acid and dimethylsuccinic acid by further oxidation.

Coriandryl chloride, $C_{10}H_{17}Cl$, is formed by passing hydrochloric acid into coriandrol as a yellowish liquid, which smells like camphor and decomposes on heating.

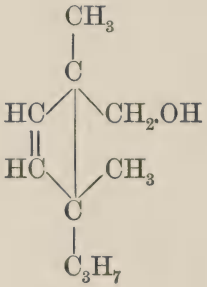
Coriandryl iodide, $C_{10}H_{17}I$, is obtained in a similar manner, and when freshly prepared is a yellowish oil, which explodes on heating even below 100°. Iodine rapidly separates out when the compound is preserved and this decomposed substance yields cymene on heating.

Coriandryl acetate, $C_{10}H_{17}.C_2H_3O_2$, is formed when coriandrol is heated with acetic anhydride and is a liquid, which boils at 228°—236° with decomposition.[2]

Tanacetyl alcohol, $C_{10}H_{18}O$, occurs in oil of tansy (*Tanacetum vulgare*), boils at 203°—205° and yields a small amount of ordinary camphor on oxidation with chromic acid. It is accompanied by *tanacetol*, $C_{10}H_{16}O$, a liquid boiling at 195°—196°, the

[1] Morin, *Compt. Rend.* xcii. 998; xciv. 733.
[2] Grosser, *Ber. Deutsch. Chem. Ges.* xiv. 2485.

smell of which faintly resembles that of the plant. It is converted into cymene by heat and is oxidized to camphoric acid by nitric acid. Acid sodium sulphite combines with it to form a crystalline compound, it reduces ammoniacal silver solution and yields tanacetyl alcohol on reduction.[1] It therefore appears to be the aldehyde of the latter, which probably has the following constitution :



ISOMERIDES AND HOMOLOGUES OF CAMPHOR.

2541 *Alantol*, $C_{10}H_{16}O$, occurs in the root of elecampane (*Inula Helenium*) and is a liquid, which smells like peppermint and boils at about 200° and is lævorotatory.[2]

Salviol, $C_{10}H_{16}O$, is found, together with camphor and terebentene, in oil of sage (*Salvia officinalis*), and is a liquid, boiling at 197°—203°.[3]

Myristicol, $C_{10}H_{16}O$, occurs, together with a terpene and cymene in the ethereal oil of nutmeg; it boils at 212°—218° and is polymerized by repeated distillation.[4]

These three compounds are converted into cymene by distillation with phosphorus chloride.

Pulegiol, $C_{10}H_{16}O$, forms the chief constituent of the oil of *Pulegium micranthum*, a plant which grows on the steppes of South Russia; it smells like peppermint, boils at 227° and absorbs hydrochloric acid, without forming a solid compound.[5]

[1] Bruylants, *Ber. Deutsch. Chem. Ges.* xi. 449.
[2] Kallen, *ibid.* ix. 154; Marpmann, *Arch. Pharm.* [3] xxv. 826.
[3] Muir and Sugiura, *Journ. Chem. Soc.* 1878, i. 292.
[4] Wright, *ibid.* 1873, 549 and 686.
[5] Butlerow, *Jahresber. Chem.* 1854, 594.

Oil of chamomile. The flowers of the false or wild chamomile (*Matricaria chamomilla*) were employed medicinally at an early date. According to Pliny and Dioscorides, the name Χαμαίμηλον relates to the odour, which is not unlike that of the apple (χαμαί, on the ground, μῆλον, apple), the plant which is found in Greece having an especially fine odour. Joachim Camerarius mentions in his *Hortus medicus et philosophicus*, 1588, that a blue oil is obtained by the distillation of chamomile with water, and recommends it as a remedy for the colic.[1] This substance, which is still employed in medicine, is a deep-blue, viscid oil, which almost takes the consistency of butter at a low temperature and has a strong smell of chamomile and a warm aromatic taste.

It contains caprinic acid, $C_{10}H_{20}O_2$, *chamomillol*, $C_{10}H_{16}O$, which is colourless, smells strongly of chamomile and boils at 150°—163° and *trichamomillol*, $C_{30}H_{48}O_3$. The last is the deep-blue, viscid portion, has a very mild smell, boils at 270°—300° and forms a deep indigo-blue vapour.[2] It also occurs, together with *absinthol*, $C_{10}H_{16}O$, boiling at 195°, in the ethereal oil of wormwood (*Artemesia absinthium*),[3] in the oil of Pilchurim beans[4] and in the oil obtained by the dry distillation of galbanum. This also contains a *triterpene*, $C_{30}H_{48}$, which is formed when trichamomillol is heated with sodium or potassium. It is colourless, boils at 255° and has a mild taste and a faint herbaceous odour.[5]

Matico camphor, $C_{12}H_{20}O$, is a homologue of camphor and occurs in the leaves of the narrow-leaved pepper (*Piper angustifolium*), which is a native of South America and is employed to staunch the bleeding of small wounds, such as those caused by blood leeches. This property is said to have been discovered by the Spanish soldier Matico, and the Matico leaves are therefore also known as *Yerba del soldato.* They contain an ethereal oil, from which the camphor separates in hexagonal crystals at a low temperature.[6] The compound after purification by recrystallization from alcohol has neither smell nor taste, melts at 94° and takes up a rotatory motion when thrown on to water.[7]

[1] Flückiger, *Pharmakognosie*, 787.
[2] Kachler, *Ber. Deutsch. Chem. Ges.* iv. 36.
[3] Beilstein and Kupffer, *Ann. Chem. Pharm.* clxx. 290.
[4] Müller, *Jahresber. Chem.* 1853, 514.
[5] Mössmer, *Ann. Chem. Pharm.* cxix. 257.
[6] *Pharmacographia*, 589.
[7] Kügler, *Ber. Deutsch. Chem. Ges.* xvi. 2841.

SESQUITERPENES, $C_{15}H_{24}$, AND SESQUICAMPHORS, $C_{15}H_{26}O$.

2542 *Cubebene* was first detected as a constituent of oil of cubebs (*Piper Cubeba*).[1] It was also found by Wallach in oil of galbanum, oil of patchouli (*Pogostemon patchouli*), oil of savin (*Juniperous sabina*), and in large quantity in the so-called *Oleum cadinum*, the tar of which is obtained in Southern France by the distillation of the wood of a species of juniper, especially *J. Oxycedrus*,[2] and is a thick, black-brown liquid. In order to separate cubebene from it, the volatile portions are distilled with steam, treated with alkali to remove phenols, dried over caustic potash and fractionated. The portion boiling between 260°—280° is then diluted with two volumes of ether, saturated with hydrochloric acid, allowed to stand for a few days and the ether then evaporated or distilled off. The chloride, $C_{15}H_{26}Cl_2$, crystallizes from the residue and is drained off, washed with a little cold alcohol and recrystallized from hot acetic ether. It is then decomposed by heating with aniline or by boiling with glacial acetic acid and sodium acetate.[3]

Cubebene boils at 274°—275° and has a sp. gr. 0·921 at 16°; it is lævorotatory and readily changes into a resin on exposure to the air.

If it be dissolved in chloroform or glacial acetic acid and then shaken up with a few drops of sulphuric acid, the liquid becomes coloured green, which soon passes into blue and is converted into red by heating. This remarkable reaction is best shown by the hydrocarbon after it has become partially converted into a resin.[4]

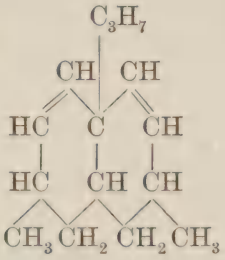
Cubebenylene chloride, $C_{15}H_{26}Cl_2$, is readily obtained by mixing cubebene with a few volumes of glacial acetic acid, and then agitating it with fuming hydrochloric acid. It crystallizes from ether in hemihedral rhombic prisms, the faces of which are striated and which show a striking resemblance to those of

[1] E. Schmidt, *Arch. Pharm.* [2] cxli. 1; *Ber. Deutsch. Chem. Ges.* x. 188.
[2] Oglialoro, *ibid.* viii. 1357.
[3] Wallach, *Ann. Chem. Pharm.* ccxxxviii. 78.
[4] If a few drops of crude oil of cubebs be shaken with twenty drops of carbon disulphide and with one drop of a cooled mixture of equal parts of concentrated sulphuric and nitric acids, the liquid becomes coloured greenish and then blue (Flückiger, *Pharmakognosie*, 874).

limonene tetrabromide, but are lævorotatory. It melts at 117°—118°.

Cubebenylene bromide, $C_{15}H_{26}Br_2$, forms snow white needles, resembling those of the chloride, which melt at 124°—125° and are decomposed by continued boiling with alcohol.

Cubebenylene iodide, $C_{15}H_{26}I_2$, crystallizes from petroleum spirit in white woolly needles, which melt at 105°—106° with decomposition and are also rapidly decomposed by boiling with alcohol. Cubebene itself has probably the following constitution.



Camphor of cubebs, $C_{15}H_{26}O$, sometimes crystallizes from the oil of old, long preserved samples of cubebene, and forms large, odourless, rhombic prisms or pyramids, which melt at 67° and are decomposed into water and cubebene when they are heated to 250° or allowed to remain in contact with sulphuric acid.

Conimene, $C_{15}H_{24}$, is obtained by the distillation of conima resin (*Icica heptaphylla*), which is used as incense in British Guiana. It is a liquid, which has an extremely pleasant aromatic odour and boils at 264°.[1]

Cedar camphor, $C_{15}H_{26}O$, occurs, accompanied by *cedrene*, $C_{15}H_{24}$, or $C_{15}H_{22}$,[2] in the ethereal oil of the Virginian cedar (*Juniperus virginiana*), and crystallizes in silky needles, which have a characteristic spicy odour. It melts at 74°, boils at 282°, and decomposes on heating with phosphorus pentoxide into water and a sesquiterpene, which boils at 237°, has a characteristic aromatic odour, quite distinct from that of cedar camphor, and a burning taste like that of pepper.[3]

Ledum camphor, $C_{15}H_{26}O$, is found, together with a sesquiterpene in *Labrador Tea* (*Ledum palustre*), and crystallizes in

[1] Stenhouse and Groves, *Journ. Chem. Soc.* 1876, i. 175.
[2] Chapoteaut, *Bull. Soc. Chim.* xxxvii. 303.
[3] Walter, *Ann. Chem. Pharm.* xxxix. 249 ; xlviii. 35.

almost odourless prisms, which melt at 104°—105° and readily sublime in needles. When it is heated to 150° with acetic anhydride, it is decomposed into water and a sesquiterpene, which boils at 264°.[1]

Patchouli camphor, $C_{15}H_{26}O$, is contained in oil of patchouli, which is obtained by the aqueous distillation of the leaves and young shoots of *Pogostemon patchouli*, a labiate plant indigenous to India, and is said to produce nervous excitement and loss of appetite when employed as a perfume. The camphor crystallizes in hexagonal prisms, melts at 59°, boils at 296°, and is decomposed by the action of hydrochloric acid or acetic anhydride into water and patchoulene, $C_{15}H_{24}$, which boils at 252°—255°.[2]

Santalol, $C_{15}H_{26}O$. The fragrant white or yellow sandalwood (*Lignum Santali album*) is derived from the Indian *Santalum album* and other species of santalum, which grow in various districts of Australia. It was highly prized at an early date in India and was formerly kept in store by druggists. At the present time it is employed in India and especially in China as incense, and also for ornaments. It contains 2—5 per cent. of an ethereal oil, which was likewise extracted at an early period and used as a perfume. This oil contains a substance named *santalal*, $C_{15}H_{24}O$, boiling at 300°, together with a smaller amount of santalol, which boils at 310° and is converted by distillation with phosphorus pentoxide into *santalene*, $C_{15}H_{24}$, boiling at 260°; santalal, on the other hand, when subjected to similar treatment, yields a hydrocarbon $C_{15}H_{22}$, which is probably identical with cedrene.[3]

Santalyl acetate, $C_{15}H_{25}.C_2H_3O_2$, is prepared by heating santalol to 150° with glacial acetic acid, and is a liquid which boils at 298° and has a fruity odour.

Volatile constituents of Paracota bark. This substance, which has already been mentioned (Part IV. p. 355), contains an ethereal oil, which may be obtained by distillation with superheated steam or by extraction with ether. It is a mobile liquid, possessing a very agreeable odour and contains the following compounds:

a-Paracotene, $C_{12}H_{18}$, is a strongly refractive liquid, which has a penetrating odour, resembling those of the oils of bitter-

[1] Trapp, *Ber. Deutsch. Chem. Ges.* viii. 542; Hjelt and Collan, *ibid.* xv. 2500; Rizza, *ibid.* xvi. 2311; xx. Ref. 562.

[2] Montgolfier, *Bull. Soc. Chim.* xxviii. 414.

[3] Chapoteaut, *ibid.* xxxvii. 303.

almonds and turpentine, boils at 160°, is dextrorotatory and does not combine with hydrochloric acid.

β-Paracotene, $C_{11}H_{18}$, has a faint but pleasant odour, boils at 170°—172°, is feebly lævorotatory and also forms no compound with hydrochloric acid.

α-Paracotol, $C_{15}H_{24}O$, is a tolerably refractive liquid, which boils at 220°—222°, has a faint odour and is lævorotatory.

β-Paracotol, $C_{28}H_{40}O_2$, boils at 236°, has a faint aromatic odour and is strongly refractive and lævorotatory.

γ-Paracotol, $C_{28}H_{40}O_2$, boils at 240°—242° and has a faint, not unpleasant odour and a very feeble lævorotation.[1]

THE DITERPENES, $C_{20}H_{32}$.

2543 *Copaivaene* is a constituent of balsam of copaiba, which is itself a mixture of resins and hydrocarbons.[2] That prepared from Para-balsam is a liquid, whose odour resembles that of the balsam; it boils at 252°—256°, and is converted by oxidation into acetic acid and asymmetric dimethylsuccinic acid,[3] $(CH_3)_2C(CO_2H)CH_2.CO_2H$. Brix discovered a diterpene in maracaibo balsam, which boils between 250°—260°, and on oxidation with chromic acid gave a small amount of terephthalic acid, in addition to acetic acid. The dry oil may be rectified over sodium without undergoing any change, whereas in the presence of moisture it is converted into a deep blue liquid, which was termed the hydrate of oil of copaiba, $C_{60}H_{98}O=3C_{20}H_{32}+H_2O$, by Brix. It boils between 252°—260° and is reconverted into the colourless oil by distillation with phosphorus pentoxide.[4]

Colophene is formed, together with other products which have already been described, by the action of sulphuric acid or phosphorus pentoxide on oil of turpentine, and also by the

[1] Jobst and Hesse, *Ann. Chem. Pharm.* cxcix. 75.

[2] Copaiba balsam is the resinous sap of several species of Copaifera, which are indigenous to South America ; it is first mentioned by a Portuguese monk, who lived in Brazil between the years 1570–1600. He states that a clear oil, highly prized for its medicinal qualities, was obtained by incisions in the bark of the Cupayba, a forest tree. It was frequently described soon after this date, and is found mentioned in the Amsterdam Pharmacopœia as Balsam. copae. yvae. The different varieties distinguished in trade are the Para Balsam, from the basin of the Amazon, and the Maracaibo Balsam, which comes from the Orinoco and Venezuela.

[3] Levy and Engländer, *Ann. Chem. Pharm.* ccxlii. 189.

[4] *Monatsh. Chem.* ii. 507.

distillation of colophonium,[1] and is an oily, viscid liquid, which boils at 318°—320°.[2]

Hevecne is obtained, together with isoprene and dipentene by the dry distillation of caoutchouc or gutta-percha, and is a faint smelling, sharp tasting liquid, which boils at about 315°.[3]

Gurjunol, $C_{20}H_{23}(OH)_2$, is a constituent of gurjun balsam or wood-oil, which is extracted from various species of Dipterocarpus in Eastern India and the Malay Islands. It is very similar to balsam of copaiba and is used in place of this, although it finds its chief application as a varnish. Gurjunol is readily soluble in alcohol and is precipitated from this solution in long, silky needles, which melt at 126°—129°. When it is boiled with sodium acetate and acetic anhydride, the acetic ether, $C_{20}H_{28}(C_2H_3O_2)_2$, is formed; it crystallizes from alcohol in small needles, melting at 74°—75°.[4]

ACIDS OF THE FORMULA $C_{20}H_{30}O_2$.

2544 *Pimaric acid* is the chief constituent of the resin of *Pinus maritima*, which is called *galipot*. It was discovered by Laurent[5] and carefully investigated by Sievert[6] and Duvernoy.[7] Versterberg was the first to show that this is not a homogeneous substance. He detected in it at least three different acids, two of which he investigated more thoroughly, although they had already been examined by Cailliot, who had not, however, succeeded in obtaining them in the pure state.[8] In order to extract them, finely divided galipot is repeatedly treated with small quantities of alcohol of 70 per cent. and finally once with 80 per cent. alcohol, the residual mass being then dissolved in hot 3 per cent. caustic soda solution. The sodium salts of dextropimaric and lævopimaric acids separate out after a few days and are recrystallized from hot water and decomposed with dilute hydrochloric acid, the precipitated acids being purified by repeated crystallization from alcohol or glacial acetic acid.

[1] Deville, *Ann. Chem. Pharm.* xxxvii. 193; lxxi. 150.
[2] Riban, *Ann. Chim. Phys.* [5] vi. 40.
[3] A. Bouchardat, *Ann. Chem. Pharm.* xxvii. 80.
[4] Brix, *Monatsh. Chem.* ii. 515.
[5] *Ann. Chem. Phys.* lxxii. 384.
[6] *Jahresber. Chem.* 1859, 508.
[7] *Ann. Chem. Pharm.* cxlviii. 143.
[8] *Ber. Deutsch. Chem. Ges.* xviii. 3331; xix. 2167.

Dextropimaric acid is insoluble in water but dissolves slightly in cold and readily in hot alcohol and glacial acetic acid, from which it crystallizes in large, rectangular plates, while it is deposited in tablets when its ethereal solution is evaporated. It is dextrorotatory, melts at 210°—211°, solidifies to a crystalline mass and may be distilled under diminished pressure. The long continued action of sodium amalgam on its alcoholic solution is without effect. When hydrochloric acid gas is passed into its uncooled ethereal solûtion, it is converted into an isomeric form, which probably consists of sylvic acid. If dextropimaric acid be heated to 250° with concentrated hydriodic acid and amorphous phosphorus, the hydrocarbon, $C_{20}H_{34}$, is formed as a viscous liquid, boiling between 320°—330°. The *dihydrocolophene*, which is obtained by the action of sodium on pinyl chloride and is a liquid resembling colophene and boiling at 321°, is probably identical with this substance.[1]

Potassium dextropimarate, $C_{20}H_{29}KO_2$, solidifies, when its hot solution is cooled, to a soap-like mass, which consists of very fine, pliable needles.

Sodium dextropimarate, $C_{20}H_{29}NaO_2 + 5H_2O$, crystallizes from water in nacreous plates and from alcohol in fine needles. It is precipitated from its solution by common salt or an excess of alkali.

Ammonium dextropimarate separates out in fine needles, when the ethereal solution of the acid is shaken up with ammonia, this being a very characteristic property.

Silver dextropimarate, $C_{20}H_{29}AgO_2$, is an amorphous precipitate, which soon changes to a heavy powder consisting of small prisms.

The calcium, barium and lead salts are all precipitates consisting of needle-shaped crystals.

Ethyl dextropimarate, $C_{20}H_{29}(C_2H_4)O_2$, is formed by the action of ethyl iodide on the silver salt. It crystallizes from alcohol in long, flat prisms, which melt at 52°.

Dextropimaryl chloride, $C_{20}H_{29}OCl$, is prepared by treating the acid with phosphorus pentachloride, and forms small prisms, melting at 64°—66°.

Lævopimaric acid is more readily soluble in alcohol than dextropimaric acid, and crystallizes in rhombic pyramids, which melt at 140°—150°. Its lævorotation is four times as great as the

[1] Montgolfier, *Ann. Chim. Phys.* [5] xix. 150.

dextrorotation of the isomeric acid; its salts resemble those of dextropimaric acid.[1]

2545 *Sylvic acid* is, according to Unverdorben, the chief constituent of colophony.[2] It has been investigated by Trommsdorff,[3] Rose,[4] and Sievert,[5] and is obtained by treating colophony with cold alcohol, and crystallizing the residue from hot alcohol, to which a little sulphuric acid should be added. Maly advanced the view that colophony does not contain sylvic acid as such. He assumed that the former substance is the *anhydride of abietic acid*, $C_{44}H_{64}O_5$, which is converted into the free acid by treatment with alcohol, and is then further changed into sylvic acid by the action of mineral acids.[6] Further investigations have however shown that abietic acid and sylvic acid only differ in degree of purity, and their formula has not yet been definitely ascertained. Liebermann and Haller, who analyzed purified sylvic acid, obtained numbers which agree with the formula of abietic acid;[7] this substance softens at 145° and melts at 162°. Valente, on the other hand, states that when colophony in powder is extracted with strong alcohol, water added until the solution becomes turbid, and this turbidity removed by the addition of a further quantity of alcohol, a crystalline mass rendered impure by resinous matter is deposited after a few days, and this may be obtained by a repetition of the process in prisms, the melting-point of which is about 160°, but is not constant; a series of analyses of products obtained in this way gave numbers, some of which agree with the formula $C_{44}H_{64}O_5$ and some with $C_{20}H_{30}O_2$. If the crystals be treated for some hours on the water-bath with dilute sodium carbonate solution, the liquid filtered and dilute sulphuric acid added, pure sylvic acid, $C_{20}H_{30}O_2$, is obtained; this substance crystallizes from alcohol in prisms and melts at 146°—148°.[8]

It appears from the above that sylvic acid, like pimaric acid, is a mixture, this supposition being confirmed by the fact that while Valente's acid is dextrorotatory, the substance prepared by Liebermann is lævorotatory.

Colophony appears to have received its name from the Ionian town Kolophon; Dioscorides mentions *κολοφωνία*,

[1] Vesterberg, *Ber Deutsch. Chem. Ges.* xx. 3248.
[2] *Pogg. Ann.* vii. 311; viii. 40 and 407; xi. 28, 230 and 393; xiv. 116; xvii. 186.
[3] *Ann. Chem. Pharm.* xiii. 109.
[4] *Pogg. Ann.* xxxiii. 42; liii. 374.
[5] *Jahresber. Chem.* 1859, 568.
[6] *Ibid.* 1861, 389; *Ann. Chem. Pharm.* cxxix. 94; cxxxii. 249; clxi. 115. See also Emmerling, *Ber. Deutsch. Chem. Ges.* xii. 1441; Kelbe, *ibid.* xiii. 888.
[7] *Ibid.* xvii. 1884; xviii. 2165.
[8] *Ibid.* xviii. Ref. 190.

and *Pix graeca* or *Colophonia* was used by the German apothecaries of the fifteenth century. It is obtained on the large scale, together with oil of turpentine, by the distillation of turpentine especially in the United States, where this great industry was commenced in the last century.[1]

Colophony forms a yellow transparent or darker coloured translucent mass, which has a conchoidal fracture, softens at 80° and melts between 90° and 100°. When heated for some time with nitric acid, it yields terebic acid, isophthalic acid, and trimellithic acid.

It is employed in the manufacture of resin soap (Vol. III. Part I. p. 693), which consists of the sodium salt of sylvic acid and the substances which occur with it. A concentrated solution of this dissolves considerable quantities of colophony, producing resin glue, which forms with water a milky fluid, employed for sizing paper.

On dry distillation colophony yields the essence of resin or resin oil, which has already been frequently referred to and is used as a lubricant, &c.

Copaivic acid is the chief constituent of copaiba resin, which remains behind when the balsam is distilled with water, and may also be readily obtained from the latter by agitating it continuously with ammonium carbonate solution and then precipitating with acetic acid. It forms large crystals, which are readily soluble in alcohol.[2]

Silver copaivate, $C_{20}H_{29}AgO_2$, is obtained as a crystalline precipitate by the addition of an ammoniacal silver solution to the alcoholic solution of the acid.

Metacopaivic acid, $C_{22}H_{34}O_4$, is contained in maracaibo balsam, and crystallizes from alcohol in plates which melt at 205°—206°,[3] and were until recently mistaken for gurjunol (p. 480).

GUAIACIC ACID, $C_{20}H_{26}O_4$.

2546 Soon after the discovery of St. Domingo, the Spaniards observed that the natives employed the wood of Hujacum

[1] Flückiger, *Pharmakognosie*, 93.

[2] Schweizer, *Pogg. Ann.* xvii. 488 ; xxi. 172 ; Rose, *ibid.* xxxiii. 35 ; liii. 372 ; Hess, *ibid.* xlvi. 324 ; Flückiger, *Jahresber. Chem.* 1867, 727.

[3] Strauss, *Ann. Chem. Pharm.* cxlviii. 153.

(*Guaiacum officinale*) as a remedy for skin diseases; this tree is also found indigenous in all the West Indian Islands, and on the south coast of South America. The wood aroused great interest in Europe since it was recommended as a remedy for syphilis (Morbus gallicus), which was at that period very prevalent. It was especially praised by Ulrich v. Hutten, who suffered from this disease, in his treatise "*Ulrichi de Hutten Eq. De Guaici medicina et morbo gallico liber unus. Monguntiae in aedibus Joannis Scheffer, mense Aprili, interregni vero quarto Anno* 1519," which was translated in 1533 by Thomas Paynel, canon of Merton Abbey, and published in London 1536.[1] In the Island of St. Domingo it is collected from the stems of the tree as a natural exudation or as the result of incisions made in the bark. In the Island of Gonave near Port-au-Prince another method is used. A log is supported in a horizontal position above the ground by two bars and each end of the log set on fire, the melted resin running from a large incision, which has previously been made in the middle.

Guaiacum resin is a brittle, dark green to brownish-black mass, which readily dissolves in alcohol. Oxidising agents such as ferric chloride or ozone, colour the solution a fine blue. When submitted to dry distillation it yields guaiol or tiglic aldehyde (Part II. p. 410), guaiacol, creosol (Part IV. p. 32), and pyroguaiacin, $C_{18}H_{18}O_3$, while on heating with zinc dust, toluene, creosol, metaxylene, paraxylene, pseudocumene and guaiene, $C_{12}H_{12}$, are formed.[2]

Guaiacum resin contains a dibasic acid, guaiacic acid or guaiaca-resin acid,[3] which crystallizes from dilute alcohol in small lustrous plates and from acetic acid in brittle needles, containing one molecule of water. It melts with loss of this at 75°—80° and gives a deep grass-green colouration with ferric chloride in alcoholic solution. On fusion with caustic potash, proto-catechuic acid is formed, while on dry distillation it yields guaiacol and a smaller quantity of pyroguaiacin.

Pyroguaiacin, $C_{18}H_{18}O_3$, crystallizes from boiling absolute alcohol in lustrous, rhombic plates, which melt at 180·5°; it boils

[1] "Of the wood called Guaiacum that healeth the Frenche Pockes and also helpeth the goute in the feete, the stoone, the palsey, lepree, dropsy, fallynge euyll, and other dyseases."

[2] Bötsch, *Monatsh. Chem.* i. 615.

[3] Hlasiwetz, *Ann. Chem. Pharm.* cxii. 182; Hlasiwetz and v. Gilm, *ibid.* cxix. 266; Hlasiwetz and Barth, *ibid.* cxxx. 346; Hadelich, *Jahresber. Chem.* 1862, 466.

at 258° under a pressure of 80—90 mm. and forms a blue solution in sulphuric acid, decomposition taking place. Its vapour density has been found to be 9·53. When it is dissolved in absolute ether and treated with potassium, the compound $C_{18}H_{16}K_2O_3$ separates out as a white powder.

Diacetylpyroguaiacin, $C_{18}H_{16}O(OCO.CH_3)_2$, is obtained by treating pyroguaiacin with acetyl chloride and crystallizes from alcohol in lustrous needles, which melt at 122°.

Guaiene, $C_{12}H_{12}$, is formed when proguaiacin is heated with zinc dust.[1] It crystallizes in large, lustrous plates, which show a faint fluorescence, have a faint but characteristic smell, melt at 100°—101° and are readily volatile, forming a vapour which has the sp. gr. 5·4. It is oxidized by chromium trioxide in acetic acid solution to *guaienequinone*, $C_{12}H_{10}O_2$, which readily sublimes in lemon-yellow needles, melting at 121°—122°; its vapour possesses a tolerably strong odour.

POLYTERPENES $(C_{10}H_{16})_n$.

2547 *Caoutchouc* had long been known to the natives of South America and India before it was heard of in Europe. It appears to have been first mentioned by Herrera (1549—1625), the celebrated Spanish historian, who relates in his account of the second voyage made by Columbus, that in Hayti a game was played with balls made of a gum, the description of which agrees with that of caoutchouc. Torquemade then relates in his *Monarquia Indiana*, 1615, that a gum is extracted in Mexico from the sap of the Uléquahil tree (*Castilloa elastica*), which is employed for preparing shoes and various water-tight articles.

Caoutchouc however first became known in Europe through Condamine, who in 1736 described his journeys in South America to the French Academy, and stated that the Indians prepare a kind of gum from the sap of the caoutchou tree, which is employed for making boots and water-tight articles and other purposes. This substance was called Hhévé in the province Esmeraldes, and wrapped in banana leaves and used for torches, which were two feet long and burnt for twenty-four hours. In France it received the

[1] Wieser, *Monatsh.* i. 594.

name *gomme elastique*, from which the term *gummi elasticum* has been derived.

The trees which yield South American caoutchouc are varieties of the species Hevea or Siphonia, as it is now usually termed. To the latter expression corresponds the Portuguese Seringa, since the caoutchouc was employed for making syringes. (*Seringa*, lat. *Sipho*).

The occurrence of caoutchouc in India was first observed by Roxburgh, the celebrated botanist, who, when staying at Calcutta in 1810, received a present from Assam of a wide-mouthed, four-sided bottle made of bamboo, which was filled with honey, and with it the information that the interior of the bamboo case was coated with the gum of a tree. This interested him more than the honey, and to his surprise he found that the coating consisted of caoutchouc. He succeeded in finding the tree from which it was obtained and described it in his *Flora Indica* as *Ficus elastica*, mentioning that caoutchouc was also employed for making candles and torches. After the annexation of Assam by the English, the East India Company offered a prize for further information concerning the tree, a company was formed for its cultivation and scientific men named by the Government to examine the question. Griffith tells us that the Indiarubber tree, known to us only as an ornamental shrub, exceeds all the trees of the tropical forest in height and expanse, and can be recognized at a distance of several English miles by its dense foliage. One of these gigantic trees had a circumference of twenty-four yards, or forty-three yards if the supporting branches be included, these forming independent roots and growing along with the parent tree. Its height was more than thirty-two yards, and it shaded a circle of 195 yards in circumference.[1]

In addition to these trees, caoutchouc is also obtained from other plants, which will be subsequently mentioned. It is widely disseminated throughout the vegetable kingdom, and, according to Schleiden, is found in all milky saps, such as those of the various species of Ficus and Papaver, so that it is also contained in opium, Cichorium, Lactuca, Sonchus, Asclepias, Euphorbia, &c. It is disseminated throughout the sap in small globules, like butter in milk, and separates like cream on standing. Many varieties of it are met with in commerce.

[1] *Ann. Chem. Pharm.* xxxi. 347.

Para caoutchouc or *Seringa fina* is the best kind and is obtained in the district of the Lower Amazon from *Siphonia brasiliensis*, while it is extracted on the upper reaches of this river and on the Rio Negro from the sap of *S. lutea et brevifolia* and in Cayenne from that of *S. elastica*.

Condamine relates that the natives make clay moulds in the form of bottles, shoes, &c., dip them in the sap and then dry them at the fire, this being repeated until a layer of the required thickness has been obtained. The mould is then broken or softened by water and removed.

An eye-witness gives the following account of the process carried out in the Para district:

"The Indians unite together generally in a pretty good number, and proceed to discover some spot in the virgin forest where there are rubber trees. As soon as they have found such a place, they cut paths through the wood to it. This is the sole difficulty experienced in procuring rubber, but it is a great one, as, owing to the fertility of the soil, the vegetation forms an almost closed mass, and every step must be gained by the axe. As soon as this labour is accomplished, they make an incision in the tree, at the height of a man's body from the ground, and arrange rude bowls of clay which hold about a tumbler full, stick the bowls to the trees a little below the incision, and collect therein the milk running out; such a bowl is filled in about three hours if the tree be fruitful. When the first cutting ceases to yield, they make a second one some distance lower down, and so on until they have exhausted the milk in the tree which is done by making in all four incisions, all at equal distances." [1]

Instead of the clay mounds, pear-shaped, spherical, or even flat pieces of wood are employed, and the Indians of the interior employ the paddles of their canoes. These are covered with a layer of clay and then employed as already described. The rubber is then dried by holding the mould in the thick smoke emitted by burning heaps of Urucari or Inaja nuts, the kernels of a palm (*Attalea excelsa et speciosa*), this smoke being supposed to impart a special quality to the goods. The Para caoutchouc comes into the market in the form of pockets or bottles of 12 cm. diameter and 5 cm. thickness, or in round pieces of the same thickness, and about 20 cm. diameter. Speckled gum, which is

[1] Hancock, *Caoutchouc or India-Rubber Manufacture*, London 1857, p. 154.

white internally, is obtained by pouring the sap on to thick earthenware plates and allowing it to dry; it forms tablets about 60 cms. square and 5—8 cms. thick. The caoutchouc which dries on the incisions in the trees and in the various vessels is made up into balls, which are called *negro heads.*

A quality which stands near in value to that from the Para district is Ceara scrap from *Manihot Glazionii*, a tree which grows on the landward side of Ceara in Brazil. In order to obtain the sap, the lower part of the stem is laid bare as far as the milk vessels, and the sap allowed to flow on to large leaves which are spread upon the ground. Here it dries in long threads or sticks, and is either sent into the market in this form or simply made up into balls.

West Indian caoutchouc is extracted in Mexico and Central America from the *Arbol del Ulé*, which has already been mentioned. In San Salvador the milk sap is mixed with water and allowed to stand until the caoutchouc has separated as a cream; the turbid water is then drawn off, and this operation repeated until it flows away clear. The mass of caoutchouc is then treated with a little alum solution, which rapidly causes it to set, after which it is pressed and dried in the shade. The same process is applied in Carthagena and other districts, such as the neighbourhood of Pernambuco in Brazil, where the juice of *Hancornia speciosa* is employed.

This variety of caoutchouc occurs in commerce in lumps or large blocks made up of a number of plates pressed together. In Panama and Nicaragua the sap of *Ipomea bona nox*, is added to the milk sap, which is thus speedily coagulated, the caoutchouc separating out as a mass smelling like fresh cheese, which is then simply pressed and made into tablets.

East Indian caoutchouc is, as already mentioned, obtained from *Ficus elastica*, a tree which is now cultivated in Upper India, Lower India, the Malay Archipelago, Angola, and Nubia. Griffith relates that in Assam the roots are laid bare, incisions made and a hole dug out underneath, in which a leaf of *Phrynium capitatum*, folded in the shape of a basin, is laid. At the present time incisions are made in the stem and the juice collected in wooden vessels; the caoutchouc is then allowed to separate, heated with water and finally well-pressed and dried. It comes into the market in lumps, which are made up of dark and light-coloured pieces kneaded together.

Borneo caoutchouc. Mr. James Howison, an English surgeon,

residing in Penang, is the authority for the following fact, taken from a memoir published by him in the year 1798: "While clearing a way through jungle with cutlasses, it was remarkable that a vine had been divided, the milk of which, drying on the blade of the weapon, possessed all the properties of American caoutchouc."[1] He described the plant, to which Roxburgh gave the name of *Urceola elastica*. It is found in Borneo, Sumatra, and the other Malay Islands, and forms a stem as thick as a man's arm and more, creeping along the ground to a great length and then rising upon the highest trees. Its small greenish flowers have the shape of a pitcher (*urceus*), and its milk-sap, as well as that of several species of Willughbeia, which are also climbing plants, and like Urceola belong to the family of Aporcynaceae, is now used for the extraction of caoutchouc, for which purpose it is simply coagulated by the addition of salt water. Borneo caoutchouc occurs in porous lumps or balls saturated with salt water. It contains the methyl ether of dambose, which has recently been recognised as identical with inosite, and has been found not to belong to the sugar group but to be hexhydroxyhexmethylene, $C_6H_6(OH)_6$.[2]

African Caoutchouc. The whole of tropical Africa is penetrated by a belt of rubber-producing climbing plants, which are used for the extraction of caoutchouc. The various species of Landolphia, yield the rubber of the Gold coast, while Lagos rubber is obtained from Ficus Vogelii the operation being carried out however with so little care that the product is only of small value. Madagascar and Mozambique, on the other hand, yield a product which stands next to the Para variety in value. It is obtained from *Vahea madagascariensis et gummifera*, climbing shrubs or trees, which are now cultivated in Java, by coagulation of the milk sap with salt water, or by simple drying. This, as has been previously mentioned, contains matezodambose, a substance closely related to inosite. It occurs in commerce in the form of balls or lumps, the best variety being reddish coloured, while the inferior qualities are black.

2548 The caoutchouc of commerce contains, according to its source, various admixtures, such as albuminoids, coloured substances, resin, mineral matter, &c. In order to purify it, it is repeatedly extracted with hot water, alcohol and ether, the

[1] Hancock, *loc. cit.* p. 153.
[2] Maquenne, *Compt. Rend.* civ. 225 and 1853.

residue dissolved in chloroform and the clear solution precipitated with alcohol. It is thus obtained as a colourless mass, resembling gum arabic.[1] Faraday, who examined a specimen of sap which Hancock had received from South Mexico in a sealed bottle, found in it 31·7 per cent. of caoutchouc, which he obtained pure by distilling the liquid with water, repeatedly shaking the separated cream with water containing hydrochloric acid, and then drying it on a porous plate. He thus obtained a colourless, opaque, elastic film, which, after the removal of all water, became transparent and showed all the properties of commercial caoutchouc. Nees von Esenbeck and Marquart allowed the liquid exuding from *Ficus religiosa* to run into ether and thus obtained a syrup, which on the addition of more ether deposited a sediment. The clear liquid decanted from this, left on evaporation a colourless, elastic mass, which still contained wax, this being however removed by boiling with alcohol.[2]

According to the analyses of Faraday and Payen, caoutchouc contains seven atoms of hydrogen to every four atoms of carbon. G. Williams however showed that it follows from the composition of its distillation-products that it is polymeric with oil of turpentine, and Bouchardat arrived at the same conclusion, which was confirmed by Adriani's analysis of purified caoutchouc. It is however very difficult to obtain a specimen of caoutchouc entirely free from oxygen (Gladstone and Hibbert).[3]

Caoutchouc has a faint but very characteristic smell; at the ordinary temperature it is soft, very elastic and tough; freshly cut surfaces are adhesive and may be firmly welded together, a property which was formerly made use of in the laboratory for the preparation of tubes, while below 0° it becomes hard and less pliable and elastic. It is tolerably hygroscopic and swells up and becomes adhesive in boiling water, this also taking place, as is well known, when it is chewed for a considerable length of time, but it regains its original properties after drying. It also absorbs alcohol and therefore swells up in this liquid more readily when the mixture is warmed. When well dried, it dissolves in ether, chloroform, benzene, oil of turpentine, oil of lavender, fused naphthalene and other hydrocarbons, as well as in carbon disulphide, its solubility in the latter being very much increased

[1] Adriani, *Jahresber. Chem.* 1850, 521. [2] *Ann. Chem. Pharm.* xiv. 43.
[3] *Journ. Chem. Soc. Trans.* 1888, 679.

by the addition of 8 per cent. of absolute alcohol.[1] It is a non-conductor of electricity and becomes strongly electrified when rubbed (Faraday). Exposed to the light it absorbs oxygen from the air and becomes brittle.[2] Spiller found in one case that the thin caoutchouc layer on the waterproof material employed for packing had gradually changed into a resin which resembled shellac, was insoluble in alcohol and had the empirical formula, $C_{10}H_{16}O_3$.[3] Caoutchouc stoppers, tubes, etc., should therefore be preserved in well closed vessels in the dark; if they become hard their pliability may be restored by exposing them first to the vapour of carbon bisulphide and then to that of petroleum.[4] If a sheet of paper be covered with a solution of caoutchouc in benzene, and the layer thus obtained exposed to the light under a photographic negative and then transferred to a lithographic stone, printer's ink will only be taken up by the portions covered by the dark parts of the negative. Caoutchouc loses its toughness and elasticity when it is allowed to remain in contact with fats or oils.

Gladstone and Hibbert have determined the specific refraction of caoutchouc, and conclude that the group $C_{10}H_{16}$ contains three double linkings and is an open chain. They have further found that pure caoutchouc does not melt in absence of air even at 200°, and that its solution in toluene retains its optical properties at this temperature. An ordinary specimen, however, commences to melt at about 120° and remains soft and adhesive after cooling, but becomes hard again when spread out in thin layers. If on the other hand it be heated to 200° it passes on cooling into a slimy mass, which does not become hard. On dry distillation it yields isoprene, C_5H_8, dipentene, $C_{10}H_{16}$ (p. 455), and heveene, $C_{20}H_{32}$ (p. 480).

Isoprene is a liquid, which boils at 37°,[5] and is probably identical with valerylene. It is converted on heating, as already mentioned, into dipentene. If it be repeatedly agitated with concentrated hydrochloric acid throughout a considerable period, diluted with water and distilled, the compounds, C_5H_9Cl and $C_5H_{10}Cl_2$, pass over and a solid substance remains, which after extraction with boiling water still contains 1·7 per cent. of chlorine, but in other respects possesses the properties and com-

[1] Payen, *Jahresber. Chem.* 1852, 638.
[2] Adriani, *loc. cit.*; Miller, *Journ. Chem. Soc.* [2] iii. 173.
[3] *Ibid.* [2] iii. 44.
[4] Hempel, *Ber. Deutsch. Chem. Ges.* xv. 914.
[5] Williams, *Journ. Chem. Soc.* [1] xv. 110.

position of caoutchouc.[1] If chlorine be passed into a solution of caoutchouc in chloroform, the compound, $C_{10}H_{14}Cl_8$, is formed which remains on evaporation in yellow scales. Bromine first produces the compound, $C_{10}H_{16}Br_4$, which on further action is converted with evolution of hydrobromic acid into a compound $C_{10}H_{15}Br_5$, which is precipitated by ether in white flakes (Gladstone and Hibbert).

2549 Caoutchouc finds numerous applications and is of the utmost value to the chemist. Liebig says in his Letters on Chemistry:

"If it be attempted to describe the progress and development of modern chemistry, a eulogy of the materials and tools which are helpful to the chemist in his work cannot be omitted. Without glass, cork, platinum and caoutchouc, we should probably not have made nearly such great advances. . . .

"By means of cork we unite wide with narrow openings and by means of cork and caoutchouc together we are enabled to construct the most complicated glass apparatus without the aid of the mechanic, or of screws and taps. . . .

"Without cork and caoutchouc we should be dependent on the mechanic in all our work. Without caoutchouc alone, apparatus would be more costly and more fragile; the chief advantage granted by both lies however in the saving of invaluable time."

After Condamine had made the scientific world acquainted with caoutchouc, the French Academy received further information concerning it from Fresneau in 1751, and from Macquer in 1768. The latter mentioned in his account the fact that small tubes might be made by spreading a solution of caoutchouc in ether over suitable moulds. It was however at first used entirely for rubbing out pencil marks and thence received the name of India-rubber in this country. Priestley, in the preface to "A Familiar Introduction to the Theory and Practise of Perspective," 1770, says, "I have since the printing of this work seen a substance which is excellently adapted for expunging pencil marks. It is sold by Mr. Nairne, opposite the Royal Exchange, who asked three shillings for half a square inch of it, but assured me that it would last for several years."

Hancock states that one ounce of bottle caoutchouc cost a

[1] G. Bouchardat, *Compt. Rend.* lxxxix. 1117.

guinea, but in spite of this high price he divined that it might be employed for more important purposes than rubbing out pencil marks, and in 1820 he cut out rings and bands of it which were used for fastening gloves, and as garters, braces, etc. In this way he obtained much waste which he could not make use of, this being also the case with the irregular masses occurring in commerce. After long-continued experiments he succeeded in finding a method by means of which caoutchouc of every description can be converted into completely homogeneous and regular masses, from which blocks, tablets, &c., may be prepared, and the wished-for articles cut out of these. The machine employed for this purpose he called a masticator.

About this period, Macintosh, chiefly with the view to the production of ammonia to be employed in the manufacture of cudbear (Pt. IV. p. 44), entered into a contract to receive for a term of years the tar and ammoniacal water produced at the Glasgow Gas Works. After the separation of the ammonia in the conversion of the tar into pitch, to suit the purposes of consumers, the oil termed naphtha is produced; and the thought occurred to him of its being possible to render this also useful, from its powers as a solvent of caoutchouc, or India-rubber. By exposure to the action of the volatile oil termed naphtha, obtained from the coal tar, he converted this substance into a waterproof varnish, the thickness and consistency of which he could vary according to the quantity of naphtha which he employed in the process.[1] He subsequently developed the further technical applications of caoutchouc in conjunction with Hancock, and the latter finally became a partner in the well-known firm of Charles Macintosh and Co., which transferred its works to Manchester.

The caoutchouc of commerce contains various mechanical admixtures. It is purified by first softening it in hot water, and then cut up into small pieces by a rapidly rotating circular knife, kept cold by a stream of water. These are then passed between rollers, also cooled by water, and the broad ragged masses thus obtained dried. In order to convert these into a homogeneous mass, the masticator, also called the kneader or wolf, is employed. It consists of a strong, fluted iron cylinder, in which a thick wooden cylinder, studded with teeth, revolves, which kneads the rubber very effectually, and thereby heats it so much that a stream

[1] Hancock *loc. cit.* Preface v.

of cold water has to be kept running on to it, the temperature of the mass rising to 70° when this was not used (Hancock). This machine has now been replaced by two rollers, which can be brought within 60-30 mm. of each other, and are heated by steam, a coherent leaf of rubber being obtained, which is crushed up and again rolled until the mass has become perfectly homogeneous, after which it is pressed in blocks. In order to colour the rubber black, lampblack from pine-wood is added, while a red colour is obtained by the addition of precipitated antimony sulphide, and a white by zinc white.

The blocks thus obtained are then cut or rolled into plates which are then worked up into tubes, cylinders, threads for elastic material, &c. Very thin sheets are prepared by moistening caoutchouc with solvent naphtha or carbon bisulphide, and spreading the resulting paste on a flat surface.

The natives of Mexico and Brazil were acquainted with the method of making articles water proof by means of the milk sap of the caoutchouc tree. A process for this purpose was patented in 1791 by Peal, who proposed to employ oil of turpentine as the solvent, but this method only became of practical importance in the hands of Macintosh. In order to prepare such materials, caoutchouc is mixed with sufficient naphtha or oil of turpentine to produce a thick varnish, with which the article in question is smeared. It is then laid on another piece covered with a thiner layer, and finally passed between rollers. Thicker materials are also made by placing a thin sheet of caoutchouc between two pieces of the stuff, while a thinner article is procured by simply laying a thin sheet on the material and passing the whole between heated rollers.

Lüdersdorf of Berlin found in 1832 that when caoutchouc is mixed with sulphur, it loses its adhesiveness, and in 1839 Goodyear took out a patent in America for sulphuretted caoutchouc, the manufacture not being further described. In 1842 however he brought into the market rubber shoes which retained their elasticity even in the cold. The action of sulphur on caoutchouc was investigated at about this time by Brockedon and Hancock, the latter of whom found that caoutchouc absorbs fused sulphur without being altered to any great extent.

If, however, the temperature be raised above the melting point, caoutchouc acquires new and very important properties. Following a suggestion of his friend Brockedon, Hancock termed this new process vulcanization. The name " owes its derivation

to the Vulcan of mythology, as in some degree representing the employment of sulphur and heat, with which that mythological personage was supposed to be familiar."

According to Payen, vulcanization takes place at 132°—140° in a few minutes. India-rubber cuttings are usually mixed with 7-10 per cent. of sulphur, and the whole repeatedly rolled out and then heated to 140°—150°.

Parkes has introduced a process by which purified india-rubber or articles made from it are vulcanized in a cold mixture of 100 parts of carbon disulphide and 2·5 parts of chloride of sulphur, and are then simply washed with lukewarm water and dried. Thick articles must be repeatedly dipped into the solution, while it is applied to waterproof fabrics by means of a sponge. An excellent method, which has been proposed by Gérard, consists in soaking the caoutchouc for some hours in a solution of potassium pentasulphide of sp. gr. 1·25 heated to 140°, after which it is washed and dried.

Vulcanized india-rubber has a grey colour, and is not adhesive. It remains very elastic and pliable even in the cold, and only swells up, without dissolving, in the solvents of ordinary caoutchouc. It contains 1—2 per cent. of sulphur chemically combined; the remainder is simply mechanically mixed with the indiarubber and can be extracted by boiling with caustic soda, a process which prevents vulcanized india-rubber from becoming hard and brittle. According to Hancock, it also becomes brittle when too much sulphur or too great a heat has been employed in its manufacture. A new industry, that of vulcanite or ebonite, was founded upon this property by Goodyear in 1853. When caoutchouc is heated to 150° with half its weight of sulphur, a plastic mass is obtained, which on cooling becomes as hard and tough as horn and can be worked in the same way as the latter. Ebonite forms an excellent isolator for electrical apparatus and becomes strongly electrified when rubbed.

The applications of vulcanized indiarubber are exceedingly numerous. It is employed, for example, in making elastic materials, surgical instruments, travelling bags, door-mats, shoes, macintoshes, life-boats, diving dresses, tires for wheels, tubes of all kinds, &c.

Vulcanite is chiefly used for making combs, penholders, knife handles, surgical and musical instruments, silver-baths for photography, cells for galvanic batteries, plates for electrical machines, casts of art objects, &c.

In the year 1886, 9265 tons (about 10 million kilos.) of caoutchouc, worth £2,202,746, were imported into England. Of this 5470 tons, valued at £1,281,499, were exported chiefly to Germany, Russia, and United the States of America.[1]

2550 *Guttapercha* occurs in the milksap of *Isonandra Gutta*, a lofty tree, which grows on the Malay peninsula, as well as on Sumatra, Borneo and other islands of the Malay archipelago, and is called percha by the natives, gutta being Malay name for gum. Sticks, riding whips, and other small articles of a similar nature, made of this substance, were brought to Europe in the seventeenth century as curiosities, but they excited no special curiosity. Dr. Montgomery, living at Singapore, was the first in 1842 to draw attention to the valuable properties of this substance, and specimens were brought to England during the following year by Joze d'Almeida and exhibited at meetings of the Royal Asiatic Society. Its value was quickly recognised; two hundredweights of it were shipped to England in 1844, while the amount imported during 1880 amounted to 65,856 cwt. (3,345,484 kilos.), worth £527,872.[2]

In order to obtain guttapercha, the trees were formerly simply felled, incisions made in the bark and the sap collected. At present the trees are tapped and the guttapercha, which separates from the sap on standing or heating, kneaded thoroughly with the hands, after which it is made into blocks and dried. Guttapercha also occurs in the saps of some other trees, which, like *Isonandra* belong to the *Sapotaceæ*. Especially rich in it is *Bassia Parkii*, a tree very widely distributed over equatorial Africa, and whose fruits, allied to shea-butter (Part I. p. 678) yield galam-butter. This discovery of a new source of guttapercha is of the highest importance, because the Malays treat their trees in so barbarous a manner that they will soon become extinct.[3] The guttapercha of trade is a reddish, marbled mass, with which sand, bits of wood, portions of bark, &c. are incorporated. It is purified on the large scale by being cut up into fine shavings, thoroughly mashed and then formed into blocks by kneading. It may be obtained perfectly pure and colourless by boiling out with alcohol, dissolving the residue in chloroform or hot benzene, if necessary decolorizing the solution with animal charcoal, and then precipitating with alcohol. Its

[1] Watson Smith, *Journ. Soc. Chem. Ind.* vi. 766.
[2] Spon's *Encyclop.* 1653.
[3] Heckel and Schlagdenhauffen, *Compt. Rend.* c. 1238; ci. 1069.

composition has been determined by Hofmann,[1] Baumhauer,[2] Adriani.[3] It dissolves in all the solvents of indiarubber.[4] At the ordinary temperature it is hard, tough, and only slightly elastic, but becomes pliable at 25°, and gradually softens on heating, being so plastic at 60° that it may be pressed into any shape or drawn out into threads or bands, and becoming adhesive at 100.° It swells up to some extent in boiling water and may then be drawn out into threads, having thus taken up 5—6 per cent. of water, which is only gradually lost on exposure to the air. At about 150° it becomes liquid and decomposes at a higher temperature, yielding the same products as caoutchouc (Williams). Like the latter, it absorbs oxygen in the sunlight, becoming brittle, and is also quickly acted upon by ozone. It may be preserved in the dark or under water, especially sea-water, without undergoing any alteration.

The guttapercha industry, like that of indiarubber, was founded by Hancock and Goodyear, who noticed that it too is rendered unchangeable in air or sun-light by the process of vulcanization, which also deprives it of the property of softening when heated. Guttapercha is employed for almost innumerable purposes, since it becomes plastic when heated and retains the form imparted to it on cooling; it is not attacked by alkalis and acids, including even hydrofluoric acid,[5] nor is it surpassed by any other substance as a non-conductor of electricity. It possesses moreover, as a conductor of sound waves, remarkable accoustical properties.

The addition of more sulphur imparts to guttapercha the properties of ebonite, and hence it is employed for similar purposes. According to Macintosh, it is also hardened by the action of concentrated sulphuric acid, after which treatment it must be very thoroughly washed with water. It is frequently mixed in various proportions with caoutchouc in order to increase its elasticity.

Bleached guttapercha serves as a filling for teeth, and is used in the preparation of sets of artificial teeth. It is also employed for surgical purposes as guttapercha paper (*Gutta lamellata*), while a solution of guttapercha in chloroform, which is known as traumaticin, finds application as a substitute for collodion.

[1] *Ann. Chem. Pharm.* cxv. 297. [2] *Journ. Prakt. Chem.* lxxviii. 277.
[3] *Jahresber. Chem.* 1860, 96. [4] Payen, *ibid.* 1852, 637.
[5] Städeler, *Ann. Chem. Pharm.* lxxxvii. 137.

2551 *Balata* is obtained from the sap of *Mimusops Balata*, a tree indigenous in Guiana and Brazil. The commercial product forms a leathery mass and contains oxygen. The pure compound isolated from this is isomeric with caoutchouc and gutta-percha,[1] and is moreover elastic like the former and becomes plastic like the latter on heating. It dissolves in the same solvents as its isomerides and can also be vulcanized.

It was formerly employed for coating telegraph wires, for isolators, surgical instruments, &c., but is now used in the United States as "chewing gum," fifty tons per annum being consumed for this purpose. Its production has recently decreased, because the tree, which grows in extremely unhealthy districts, is no longer cultivated and is gradually dying out.[2]

Helenite was found among the earth thrown up from one of the shafts at the Ropa petroleum works. It occurs in thin laminæ, 10—15 cm. long, and 4—5 cm. wide, which, after treatment with ether to remove liquid hydrocarbons, are white and faintly translucent, becoming elastic when immersed in water. On heating it gives off vapours having the smell of those of Para-rubber. It is soluble in the same solvents as india-rubber, and can also be vulcanized, so that it appears to be a fossil india-rubber.[3]

Coorongite is the name given to a rubber-like mass, which was discovered in 1866 in Coorong, in South Australia, where it occurs in tolerably thick layers, lying on the sand. Nothing is definitely known as to its origin, but it is probably a fossil resin.

When submitted to dry distillation it yields about 82 per cent. of liquid and gaseous hydrocarbons.[4]

Dammar Resin is derived from the Amboyna pine, *Dammara orientalis*, which grows in the same countries as the guttapercha tree. The natives employ it as incense and for candles, which are made by enveloping the powder with palm leaves or filling it into pines of bamboo. In this country it is used for varnishes and lacquers. It contains a number of oxygenated compounds, accompanied by *dammaryl* ($C_{10}H_{16}$), which may be isolated by extracting the resin with hot alcohol, treating the residue with ether, concentrating this solution and pouring it into water. It

[1] Sperlich, *Jahresber. Chem.* 1869, 789.
[2] Spon's *Encyclop.* 1635.
[3] Nawratil, *Ber. Deutsch. Chem. Ges.* xvi. 2312.
[4] *Jahresber. Chem.* 1872, 1147; Heinzerling, *Kautschuk- und Guttapercha-waaren.*

is thus obtained as a lustrous amorphous powder, which melts at 190° and absorbs oxygen from the air.[1]

Fichtelite occurs in a peat bed near Redmitz in the Fichtelgebirge, and is also found in fossil pines in the form of scales or flat needles; it has also been met with in a peat-bog at Franzenbad and in Denmark. It crystallizes from alcohol in monoclinic tablets, which melt at 46° and distil above 320° without decomposition.[2]

Hartite, which occurs in deposits of brown coal, is very similar to fichtelite, but melts at 74°.[3]

A number of other fossil polyterpenes are also known.

[1] Dulk, *Journ. Prakt. Chem.* xlv. 36.
[2] Bromeis, *Ann. Chem. Pharm.* xxxvii. 304; Steenstrup and Forchhammer, *ibid.* xli. 42; Clarke, *ibid.* ciii. 326.
[3] Haidinger, *Pogg. Ann.* liv. 261; Schrötter, *ibid.* lix. 43.

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